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EUGENOL AND SOME OF ITS DERIVATIVES.

BY G. B. FRANKFORTER AND MAX LANDO.

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THE eugenol with which the following experiments were made came from the factory of C. A. F. Kahlbaum, of Berlin. According to statements from the factory, it should have been pure. An examination showed, however, that it was not. It contained certain organic impurities, a considerable quantity of water, the result, no doubt, of steam distillation, and a small amount of inorganic matter.

The oil used in experimenting was distilled by steam, and then *in vacuo*. By a second distillation *in vacuo*, the oil was obtained practically colorless. The physical properties were immediately taken. The following is a comparison of the properties of the purified oil, with the properties as given by Tiemann and others:

BOILING-POINT.

Tiemann 247° C.
Gladstone 252° C. ..... Found 244.5° C.
Williams 251° C.

SPECIFIC GRAVITY.

Williams, 1.068 at 14° C.
Church 1.066 at 15° C. ..... Found 1.0689 at 20° C.
Wasserman 1.063 at 18.5° C.
Tiemann-Kraaz 1.0703 at 14° C.

Index of refraction 1.540	Found	1.54437
Mol. heat of combustion 1286.9	"	1304 calorie
Specific heat	"	0.5024

Metallic Salts of Eugenol.—Eugenol forms salts with all of the alkali metals. These salts have the general properties of the phenolates. They are, however, less stable than the latter. They slowly decompose on exposure to the air. In this decomposition, carbonates of the metals are formed, and the eugenol is partially oxidized into a light-colored amorphous powder, which seems to have a definite composition.

Lithium Eugenolate, $C_{10}H_{11}O_2Li$.—Lithium hydroxide or even lithium carbonate forms with eugenol a well-crystallized salt with the general properties of sodium and potassium eugenolate. By treating eugenol with a concentrated solution of lithium hydroxide, an almost white, amorphous mass is formed. By using an excess of eugenol, filtering, and washing with ether, the pure salt is readily obtained. By dissolving in alcohol and evaporating *in vacuo*, the salt was obtained in crystal form. *In vacuo*, or in an atmosphere of hydrogen, the salt has been kept for several months. The analysis gave: C, 70.09; H, 6.41; Li, 4.01. Calculated for $C_{10}H_{11}O_2Li$: C, 70.59; H, 6.47; Li, 4.12.

Lead Eugenolate, $(C_{10}H_{11}O_2)_2Pb$.—Eugenol boiled for some time with litharge, slowly dissolves it. On treating the solution with absolute alcohol, a light-colored substance precipitates out, while the alcohol dissolves the excess of eugenol. After washing carefully with alcohol, the substance appeared almost white. The substance was further purified with ether and examined. It appeared to be a semi-crystalline substance with a very high melting-point. Like all other salts, it decomposes in water, but much more slowly than the lithium and sodium salts.

The analysis gave 38.88 per cent. Pb; calculated, 38.83.

Several analyses of the substance, after it had been made some time, showed that it readily decomposed. Analyses of this substance treated with water, indicated that, perhaps, a basic salt is formed. As in the case of lithium and sodium salts, after exposure to the air, the eugenol undergoes some deep-seated change, leaving a solid amorphous substance after the metals have been removed. Further investigation of these salts is being made.

The Bromine Compounds of Eugenol.—The bromine compounds

of eugenol have been studied several times. Cahours[1] and Wasserman first examined them, and prepared several compounds. Most of those prepared, however, were the methyl and ethyl eugenol compounds, owing, as is stated, to the extreme difficulty of obtaining the simple bromides in pure form. Later, Chasanowitz and Hell[2] prepared a tetra-brom compound, a dibrom-eugenol dibromide, $C_6HBr_2(OCH_3)(OH)C_3H_3Br_2$, and by heating this compound with zinc dust in alcoholic solution, a dibrom-eugenol was obtained.

The following experiments were begun on bromides, not with the idea of studying them but of using them as material for substitution products. It was soon observed that the results did not correspond entirely with the compounds above mentioned, and the compounds were, therefore, more carefully studied. From a great number of experiments it would seem that the reaction of bromine on eugenol varies with the conditions under which it is added. As briefly noted by Cahours, if bromine is added directly to eugenol, a most violent reaction takes place, resulting in a decomposition of much of the eugenol to carbonaceous matter, and liberating a large amount of hydrobromic acid. Several trials, even in a freezing-mixture, failed to yield anything definite, except a black, insoluble, uninviting, carbonaceous mass, and large volumes of hydrobromic acid. Different methods of preparing the bromide were then tried.

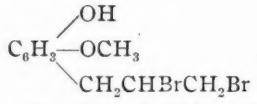
Eugenol was finally dissolved in an excess of chloroform, cooled to below zero, and bromine very slowly added. A reddish brown liquid was formed which, upon evaporating off the chloroform, left a dark, amorphous mass. This substance refused to crystallize from any of its solvents. The mass was then subjected to distillation under diminished pressure. A small quantity of a reddish liquid was obtained at 80°–140°. At 180°-190° C. dense fumes were liberated, and there was evidence of vigorous decomposition. The whole mass was then subjected to steam distillation, when a small amount of oil passed over. It had somewhat the odor of eugenol. The bromide remained in the flask as a light yellow semi-solid, which, on standing, became an almost white, solid, granular substance.

Several trials, under the above conditions, indicated that the reaction was almost quantitative. The bromide was made a number of times, yielding the following results:

[1] *Ann.*, **108**, 320.
[2] *Ber.*, **18**, 823.

50 grams of eugenol with 50 grams of bromine gave 100 grams of bromide.
25 " " " 25 " " " 50 " "
20 " " " 20 " " " 40 " "
10 " " " 10 " " " 20 " "
5 " " " 5 " " " 10 " "

These results, which corresponded with results already obtained, led us to assume with Chasanowitz and Hell, that the substance in hand was eugenol dibromide,



However, to make sure that the substance was a dibrom compound, an analysis was made, which gave 49.07 per cent. Br; calculated for $C_{10}H_{12}O_2Br_2$, 49.38.

The Action of Potassium Hydroxide on the Dibromide.—Potassium hydroxide readily reacts upon the bromide. A strong solution of the hydroxide produces a dark, resinous mass, which seems to be a decomposition product of the bromide. With a dilute solution of the hydroxide, however, the reaction is entirely different. In the cold, the bromide dissolves to a reddish colored liquid, but on heating for some time, a white, amorphous substance is precipitated. The white precipitate was removed, washed with enough alcohol to remove the excess of hydroxide, and dissolved in chloroform. After filtering and evaporating off the chloroform, a light-colored amorphous powder was left. The powder was redissolved in chloroform, filtered through a little clean animal charcoal, and again evaporated. The powder obtained was almost white, and slightly crystalline. It began to change at 78° C., and was completely melted at 80° C. An examination of the substance showed that it still contained bromine, while the hydroxide solution also showed the presence of bromine.

In order to determine how much of the bromine had been removed, bromine determinations were made of the substance, and of the hydroxide solution. Several determinations were made under different conditions, chiefly with the object of removing, if possible, all of the bromine. Analyses showed, however, that even after boiling several hours in a potassium hydroxide solution, only one half the bromine could be removed.

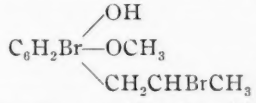
The following are some of the bromine analyses made of the precipitate and of the hydroxide.

1. 1.4844 grams dibromide lost to potassium hydroxide 0.8781 gram AgBr.
2. 0.5164 " " " " " " 0.2984 " "
3. 0.7932 " " " " " " 0.4582 " "
4. 1.204 " " " " " " 0.6869 " "

	Calculated for $C_{10}H_{12}O_2Br_2$.	Found.			
		1.	2.	3.	4.
One atom Br=24.69.....	25.44	24.82	24.71	24.41	

The substance from which the analyses were made was prepared at different times.

These analyses would indicate that the two bromine atoms are entirely different as regards the affinity with which they are held, and hence indicate that the one atom of bromine which cannot be removed is in the ring.[1] As already stated, hydrobromic acid is liberated in the presence of bromine, or upon adding the bromine rapidly. A reasonable explanation would be to assume that the bromine first enters the ring, and by substitution liberates hydrobromic acid, which in turn combines with the propylene group. This explanation is strengthened by the readiness with which hydrobromic and hydrochloric acids are liberated, in the formation of the higher bromides and chlorides. The original dibromide, then, is not eugenol dibromide, but brom-eugenol bromide,



Brom-eugenol Hydroxide, $C_{10}H_{13}O_3Br$.—The white, amorphous powder obtained by heating the dibromide with dilute potassium hydroxide was digested with dilute hydrochloric acid, dried, washed with a little alcohol and ether, and repurified from chloroform. The substance was almost white, but appeared to be amorphous. The m. p. was 79°-82° C. An analysis gave 30.3 per cent. Br; calculated for $C_{10}H_{13}BrO_3$, 30.65.

This substance is now under further examination.

Tribrom-eugenol Bromide, $C_{10}H_{10}O_2Br_4$.—As stated by Chasanowitz and Hell,[2] the tetrabrom-eugenol is a dibrom-eugenol dibromide, two atoms in the propylene group, and two in the benzene ring. From the peculiar reaction of the dibrom compound we were led to study the tetrabrom compound in the same way with regard to the position of the bromine atoms. In this case not only potassium hydroxide, but also silver nitrate,

[1] The action of bromine on coumarin, *J. Chem. Soc.*, **23**, 368.
[2] *Ber. chem. Ges.*, **18**, 824.

silver hydroxide and zinc were used for the removal of a part of the bromine. In each case, however, only one-fourth of the bromine could be removed. A study of the properties of the tetra compound indicated that it is not identical with that described by Chasanowitz and Hell.

This bromide is given as insoluble in ether, whereas the bromide in hand, is quite soluble. One gram is completely dissolved in 14.2 grams of ether. It is insoluble in water, but soluble in dilute potassium hydroxide. The bromide in hand was prepared by dissolving the eugenol in ether, and cautiously adding 3 parts by weight of bromine to the well-cooled solution, taking care that the temperature should not rise above zero for several hours after the bromine has been added. On evaporating off the ether, a reddish, crystalline substance was left. On washing with cold alcohol it became almost white. The substance is soluble in hot alcohol, from which it crystallizes in large, triclinic crystals. The crystals melt at 118.5° C.

The analysis of the crystallized substance gave: C, 24.5; H, 3.5; Br, 66.89. Calculated for $C_{10}H_{10}Br_4O_2$: C, 24.90; H, 2.1; Br, 66.66.

The crystals were so perfect that they have been measured, and were shown to belong to the triclinic system.

The Action of Potassium Hydroxide on the Tetrabromide.—By heating the tetrabromide with a dilute solution of potassium hydroxide, a reaction quite similar to that between the reagent and the dibromide takes place. Only one quarter of the bromine could be removed, as indicated by the following analyses

1. 0.5 gm. bromide lost to potassium hydroxide by boiling 0.0831 gm. Br.
2. 0.5 " " " " " " " " 0.0831 " "

	Calculated for $C_{10}H_{11}Br_4O_2$.	Found. 1.	Found. 2.
One atom Br =	16.59	16.52	16.52

It is evident here again that, contrary to the general rule, only one bromine atom has entered the propylene group, while the other three have entered the ring. This may be explained as analogous to the reaction with the dibromide. In this case, however, a large amount of hydrobromic acid is liberated.

Tribrom-eugenol Hydroxide, $C_{10}H_{11}O_3Br_3$.—The white precipitate formed on warming the tetrabromide with dilute potassium hydroxide, was filtered off, purified and examined. It is soluble in

chloroform, but insoluble in almost all other solvents. From chloroform it is obtained as an almost white, amorphous powder, with a melting-point of 137° C. One gram of the tetrabromide gave 0.8746 gram of the tribrom compound, an almost quantitative reaction. Combustion of the tribrom compound gave: C, 28.55; H, 2.7. Calculated for $C_{10}H_{11}O_3Br_3$: C, 28.6; H, 2.62.

The Action of Chlorine on Eugenol.—Chlorine, like bromine, combines readily with eugenol, but to obtain definite compounds is a much more difficult problem than in the case of bromine. After several fruitless attempts to prepare the di- and tetra-compounds, chlorine was passed into eugenol, dissolved in chloroform and cooled by a freezing-mixture, for several days, and until no more chlorine was absorbed. At the end of the process, the eugenol had absorbed considerably more than its own weight of chlorine. A weighed quantity, 51 grams of eugenol, when finally saturated, absorbed 62 grams of chlorine. In the beginning of the reaction the solution took on a golden yellow color. Some of this solution was removed and examined, and as usual, proved a yellowish, waxy mass on evaporating off the chloroform. Later in the process the solution appeared more of a reddish color. Finally, the saturated solution was removed and evaporated, when a reddish mass remained. This was subjected to steam distillation, a process which removed a small quantity of a high-boiling liquid, not unlike eugenol in appearance and in odor. After the volatile substance was removed, the whole mass was dried, and allowed to stand for some time in a desiccator over sulphuric acid. It finally appeared crystalline, but retained its reddish color. It was further purified by dissolving in ether, and filtering through a little clean animal charcoal. From this purified substance the analyses gave: C, 35.21; H, 2.64; Cl, 51.80, 52.09, 52.12. Calculated for $C_{10}H_9Cl_5O_2$: C, 35.45; H, 2.65; Cl, 52.44.

The Action of Zinc Dust on the Pentachloride.—Eugenol pentachloride was dissolved in 90 per cent. alcohol, an excess of zinc dust added, and digested for two days. The whole mass was heated on a water-bath until the alcohol was evaporated. The salts were then taken up with water and filtered. The chlorine, as zinc chloride in the filtrate, was then determined with the following results:

1. 0.2080 gram of pentachloride lost 0.0493 gram of Cl.
2. 0.2005 " " " " 0.0407 " " "

Calculated for $C_{10}H_9Cl_5O_2$.	Found.	
	1.	2.
Cl_2=20.95	23.74	20.3

Zinc Tetrachlordi-Eugenolate, $C_{20}H_{16}Cl_6O_4Zn$.—The substance left after filtration consisted of a chlor-eugenol compound of zinc and an excess of zinc. This substance was treated with alcohol and filtered. After evaporating off the alcohol, the zinc compound was obtained as a white powder, which refused to crystallize, and had an unsatisfactory melting-point. Analyses made of the amorphous powder gave: Cl, 33.6, 32.60, 33.99; Zn, 9.7, 10.21. Calculated for $C_{22}H_{16}Cl_6O_4Zn$: Cl, 35.59; Zn, 10.88.

The substance decomposes readily, and great difficulty was experienced in purifying it.

Trichlor-eugenol Hydroxide, $C_{10}H_{11}Cl_3O_4$.—Pentachlor-eugenol was digested in dilute potassium hydroxide until the reddish color had changed to a green. During the process, a very peculiar odor was given off. When the solution was brought to a boil, it again changed color, and a flocculent precipitate formed. This was filtered off and examined. It had a reddish color, and had lost part of its chlorine. Analyses proved unsatisfactory, owing to the presence of some organic matter. The precipitate was then dissolved in alcohol and allowed to evaporate slowly, when an amorphous, brown powder remained. Several attempts to crystallize it failed. The purified powder was analyzed, and gave 35.54 per cent. Cl; calculated for $C_{10}H_{11}Cl_3O_4$, 35.29 per cent.

This substance is at present under further examination.

Thiodi-eugenol Dichloride, $C_{20}H_{24}O_4SCl_2$.—When sulphur dichloride is brought into contact with eugenol, a violent reaction takes place, resulting in a complete decomposition of the eugenol. If eugenol is dissolved in some solvent like ether or chloroform, and sulphur dichloride cautiously added, a reaction takes place, raising the temperature of the ether to the boiling-point, unless the chloride is added very slowly. The chloride was added under different conditions, evidently yielding in each case a different compound. If equal parts of eugenol and chloride are brought together in ether, the ether boils vigorously, and on evaporating, there is left an oil with somewhat the odor of eugenol. The substance contains both sulphur and chlorine. If, however, the chloride is added in slight excess to an ether solution, cooled to zero, and kept at that temperature for some time, a bright red

compound slowly precipitates out from the ether solution. This substance is readily freed from any traces of chloride or eugenol by treating with excess of ether, which readily dissolves either of the two substances. The red substance was carefully purified and analyzed. There was found: C, 55.78; H, 6.17; Cl, 14.42. Calculated for $C_{20}H_{24}O_4SCl_2$: C, 55.68; H, 5.57; Cl, 16.47; S, 7.42.

A determination of sulphur ran too high, giving results which at first led us to believe that the substance in hand was a dithio compound. Later experiments indicated, however, that the substance was not quite pure. The reaction is at the present time under further examination.

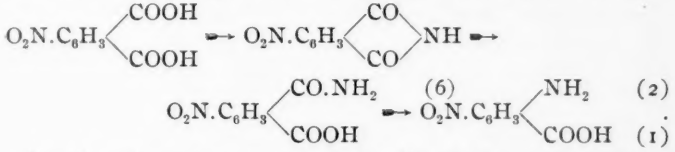
UNIVERSITY OF MINNESOTA.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 106.]

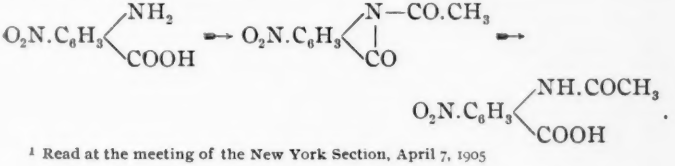
THE SYNTHESIS OF 5-NITRO-4-KETODIHYDROQUINAZOLINES FROM 6-NITRO-2-AMINOBENZOIC ACID, 6-NITRO-2-ACETYLAMINOBENZOIC ACID, AND FROM THE CORRESPONDING NITRO ACETYLANTHRANIL.[1]

BY MARSTON TAYLOR BOGERT AND VICTOR JOHN CHAMBERS.

3-NITRO-*o*-PHTHALIC acid was converted into the imide, and the latter then changed to 3-nitrophthal-1-amic acid and to 6-nitro-2-aminobenzoic acid by the usual reactions with bromine and alkali:



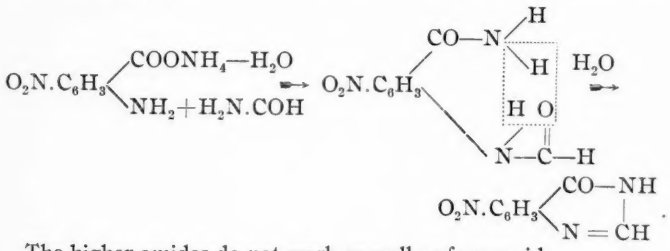
By the action of excess of acetic anhydride upon this nitroanthranilic acid, the nitro acetylanthranil was obtained, which, by crystallization from boiling water, was hydrolyzed to the nitro acetylanthranilic acid:



[1] Read at the meeting of the New York Section, April 7, 1905

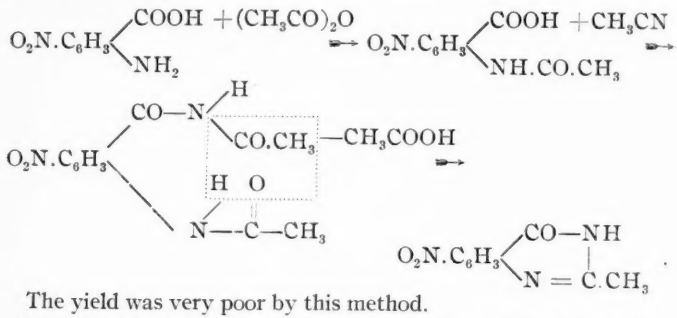
From the nitro anthranilic acid, its acetyl derivative, and the nitro acetylanthranil, quinazolines were readily obtained as follows:

I. By heating the ammonium salt of the nitro anthranilic acid with formamide[1]—



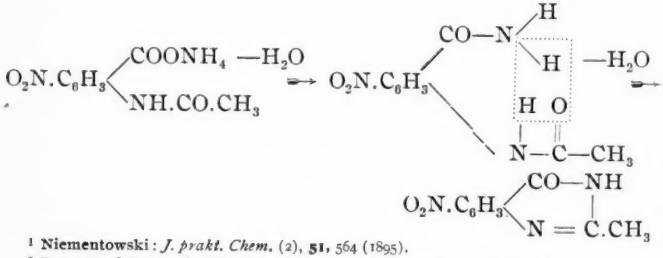
The higher amides do not work so well as formamide.

II. By heating the acid in sealed tubes with acetic anhydride and acetonitrile[2]—



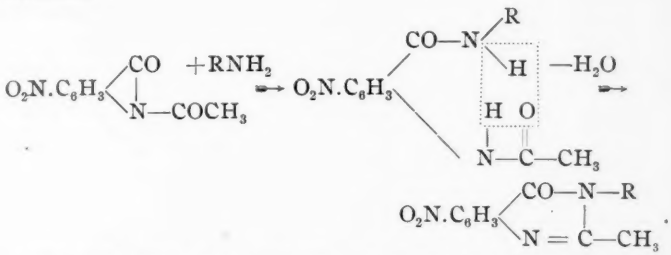
The yield was very poor by this method.

III. By heating the ammonium salt of the acetylanthranilic acid[3]—



[1] Niementowski: *J. prakt. Chem.* (2), **51**, 564 (1895).
[2] Bogert and Gotthelf: This Journal, **22**, 129, 524 (1900); **23**, 611 (1901).
[3] Bischler and Burkart: *Ber. chem. Ges.*, **26**, 1349 (1893).

IV. By the action of primary amines upon the nitro acetylanthranil[1]—



The yields by this method are nearly quantitative, and the products are very pure.

Of the four possible Bz-nitro-2-methyl-4-ketodihydroquinazolines two have been known since 1891.

Of these, the 6-nitro compound was first obtained by Dehoff,[2] by the direct nitration of 2-methyl-4-ketodihydroquinazoline. The position of the nitro group in Dehoff's product was established by Thieme's synthesis of the same substance from the ethyl ester of 5-nitro-2-acetaminobenzoic acid and alcoholic ammonia at 170°.[3] By a similar process, using the ester of 3-nitro-2-acetaminobenzoic acid, Zacharias[4] prepared the 8-nitro isomer.

In the present paper, the 5-nitro-2-methyl-4-ketodihydroquinazoline is described, and we are engaged now in the preparation of the 7-nitro isomer, to complete the series.

These nitro quinazolines may be reduced to amino quinazolines, and the latter are also being studied in this laboratory. We would, therefore, like to reserve this field for further investigation.

EXPERIMENTAL.

6-Nitro-2-aminobenzoic Acid.—3-Nitro-*o*-phthalic acid was prepared by the direct nitration of phthalic anhyride.[5] Care should be taken that the first reaction does not become too violent, or the phthalic anhydride may be entirely destroyed. The yield of pure 3-nitro acid is usually about one-third the weight of phthalic anhydride used. More may be recovered from the mother-liquors by

[1] Anschütz, Schmidt and Greiffenberg: *Ber. chem. Ges.*, **35**, 3480 (1902).

[2] Dehoff: *J. prakt. Chem.* (2), **42**, 347 (1890).

[3] Thieme: *Ibid.*, **43**, 473 (1891).

[4] Zacharias: *Ibid.*, **43**, 441 (1891).

[5] Miller: *Ann. Chem.* (Liebig), **208**, 223 (1881); Bogert and Boroschek: This Journal, **23**, 742 (1901).

concentration, but it is apt to be contaminated with the 4-nitro acid.

One molecule of the nitro acid is dissolved in a small amount of hot water, the solution neutralized with ammonia, any excess of ammonia boiled out, and a second molecule of the nitro acid then added. On cooling, the acid ammonium salt separates in quantitative yield. By the action of heat upon this acid ammonium salt, the imide is obtained in the calculated quantity.[1] It is best crystallized from a mixture of alcohol and acetone (1 : 2). The preparation of the imide from the anhydride, as recommended by Kahn,[2] works all right for small amounts, but we have found it much less satisfactory for the preparation of large amounts. In our experience, it takes much longer to get 500 grams of the pure imide from the anhydride than from the acid ammonium salt.

From the imide and caustic potash, the amic acid is readily prepared by Kahn's method.[3] If the solution of the potassium salt of the amic acid be well cooled before acidifying with hydrochloric acid, the amic acid separates immediately as a crystalline powder of pale brownish tint. By the addition of salt to the mother-liquor, more amic acid is separated, bringing the total yield up to 80-90 per cent. of the weight of imide used.

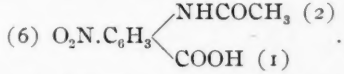
The amic acid is changed to the 6-nitro-2-aminobenzoic acid by the action of bromine and caustic potash, as described by Kahn.[4] It is, of course, essential to keep the solutions ice-cold until the necessary amount of alkali and bromine has been added. The cold solution should then be placed directly upon a boiling water-bath, and heated up as rapidly as possible, the close of the reaction (thirty to forty minutes) being indicated by the solution turning a rich red color, when it should be cooled down rapidly in an ice pack and carefully acidified with the calculated amount of hydrochloric acid. The amino acid then separates in beautiful yellow needles, which are practically pure. If the heating and cooling proceed slowly, the product will be darker in color and smaller in amount. When not perfectly pure, its tendency is to separate in a granular condition. In case the acid does not separate from the cold solution on shaking, it can generally be precipitated by the addition of a little salt. The yield is 80 to 85 per cent. of the weight of amic acid taken.

[1] Bogert and Boroschek: *Loc. cit.*, p. 747.
[2] Kahn: *Ber. chem. Ges.*, **35**, 3866 (1902).
[3] Kahn: *Loc. cit.*, p. 3868.
[4] Kahn: *Loc. cit.*, p. 3863.

A further crop of less pure material may be recovered from the mother-liquors by adding more salt and stirring with a turbine for six to eight hours, or by extracting with ether or ethyl acetate, but the amount thus recovered does not pay for the time expended.

We have also tried the method of Seidel and Bittner,[1] by which the imide is converted directly into the amino acid by the action of caustic soda and bleaching-powder, without separation of the intermediate amic acid, and have found it much less satisfactory than the above.

6-Nitro-2-acetaminobenzoic Acid,



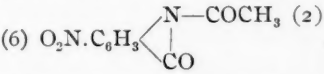
—Powdered nitro acetylanthranil is added to gently boiling water until no more is easily taken up. On cooling, nitro acetylanthranilic acid crystallizes out. It may be recrystallized from water in the same way, or from ethyl acetate.

It is obtained in large well-formed prismatic crystals, melting with decomposition at 212°-214°, according to the rapidity of the heating. A portion was kept at a temperature slightly above its melting-point for some time, but no nitro acetylanthranil could be detected in the resultant black tarry mass. The substance is soluble in water, and slowly hydrolyzed by it on long boiling. It is easily soluble in cold acetone, hot alcohol or hot ethyl acetate, slightly soluble in warm chloroform or benzene, insoluble in ether or petroleum ether.

Calculated for $C_9H_8O_5N_2$: N, 12.5. Found: N, 12.8.

Seidel and Bittner[2] attempted to prepare this compound by the direct action of acetic anhydride upon the nitro anthranilic acid, but failed to obtain a pure product.

6-Nitro Acetylanthranil,



—This results when the nitroanthranilic acid is boiled for a few minutes with excess of acetic anhydride. On cooling, it separates in pale yellow prisms. If the nitro anthranilic acid used was perfectly pure, these crystals will be but faintly colored and prac-

[1] Seidel and Bittner: *Monatsh. f. Chem.*, **23**, 421 (1902).

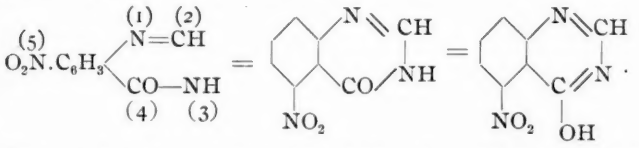
[2] Seidel and Bittner: *Ibid.*, p. 427.

tically pure. The substance may be re-crystallized from acetic anhydride or from ethyl acetate. If the crystallization from ethyl acetate causes any hydrolysis (which is quite likely to occur unless the acetate be perfectly dry), a further crystallization from acetic anhydride will remedy the difficulty. By evaporating the mother-liquor, at ordinary temperature, in a current of dry air, an additional amount may be obtained. The total yield is nearly theoretical.

When pure, the anthranil forms large colorless plates or prisms, m. p. 155°-156° (corr.), stable in dry air, slowly hydrolyzed in moist air, rapidly by boiling with water, to nitro acetylanthranilic acid. It is soluble in cold acetone or boiling chloroform, slightly soluble in hot carbon tetrachloride, ether, petroleum ether or benzene. It reacts very readily with primary amines, with formation of substituted anthranilamides, which easily condense to quinazolines.

Calculated for $C_9H_6O_4N_2$: C, 52.4; H, 2.9; N, 13.6. Found: C, 52.4; H, 3.1; N, 13.4, 13.4.

5-*Nitro*-4-*ketodihydroquinazoline*,



—The powdered ammonium salt of the nitroanthranilic acid is treated with slightly more than one molecule of formamide and heated for four or five hours at 150°-160° in a paraffin-bath, or until the liquid mixture becomes semi-solid. Ammonia is evolved during the reaction. When cold the mass is washed with a little cold water, dissolved in a large volume of boiling water, the solution bone-blacked and filtered hot. From the filtrate, on cooling, the quinazoline separates in a mass of needles. Recrystallized from hot water it forms beautiful colorless needles, melting at 255°-256° (corr.), with decomposition.

It is fairly soluble in boiling water, alcohol or acetone, sparingly soluble in the cold, practically insoluble in hot or cold ether, chloroform, petroleum ether or benzene. It dissolves readily in solutions of the caustic alkalies or of ammonia, and is reprecipitated from these solutions by carbon dioxide or by dilute acids.

Boiled with concentrated caustic potash no ammonia is split off.

Calculated for $C_8H_5N_3O_3$: C, 50.3; H, 2.6; N, 22. Found: C. 50.5; 50.3; H, 2.9, 2.8; N, 22.2.

Dimorphism of 5-Nitro-4-ketodihydroquinazoline.—When a hot aqueous solution of the quinazoline is allowed to cool quickly only fine needles separate at first, but small prisms soon appear on the walls of the vessel. On standing, the needles gradually disappear and the prisms on the side walls increase. This change is slow at room temperature, twenty-four to thirty-six hours being necessary usually for its completion. On the boiling water-bath the same change may be completed in three to four hours. The needles, when dry, crumble to a fine granular powder on the slightest touch. The prisms show the same melting-point and solubilities as the needles, and are easily reverted to them by solution in boiling water and rapid cooling. The prisms always show a pale green color, even when the needles from which they were obtained were perfectly colorless.

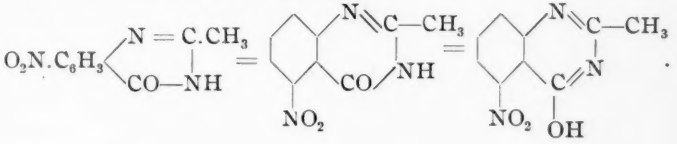
Chloride.—The addition of concentrated hydrochloric acid to the quinazoline changes it to a white amorphous salt which is soluble only in large excess of the hot concentrated acid. On cooling, it separates from such a solution as a white, microcrystalline powder, melting with decomposition at 240°–246°. When boiled with water, needles of the free quinazoline are obtained.

Chlorplatinate.—The quinazoline appears to dissolve more easily in hot concentrated hydrochloric acid when chlorplatinic acid is present. When such a solution cools the chlorplatinate separates in yellowish red crystals.

Calculated for $(C_8H_7O_4N_3.HCl)_2PtCl_4$: Pt, 24.5. Found: Pt, 24.4.

Nitrate.—The quinazoline dissolves rapidly in warm dilute nitric acid (1 : 4), and, on cooling, heavy, prismatic needles separate, which melt at about 218° with decomposition. When boiled with water the free quinazoline is regenerated.

5-Nitro-2-methyl-4-ketodihydroquinazoline,



—This was prepared by the following methods:

(1) *From 6-Nitro-2-aminobenzoic Acid, Acetic Anhydride and Acetonitrile.*—Five grams of the nitro anthranilic acid, 3 cc. of acetic anhydride, and 3 cc. of acetonitrile were heated together in a sealed tube for six hours at 160°-170°. On opening the tube no pressure was evident. The tube contained a dark crystalline mass with a small amount of a reddish liquid. The mixture was repeatedly extracted with small amounts of warm ether. The residual reddish brown, granular mass was dissolved in potassium hydroxide solution, and precipitated with carbon dioxide. The precipitate obtained was dark-colored and flocculent. It was dissolved in warm alcohol and the solution bone-blacked. From the filtrate, on cooling, the quinazoline crystallized in fine white needles melting at 277°-279° (corr.), with decomposition. The yield was small. The ether extracts mentioned above contained nitro acetylanthranil and *m*-nitraniline, together with a small amount of a substance insoluble in alkali (possibly the quinazoline which would result from a combination of the anthranil and nitraniline).

(2) *From the Ammonium Salt of 6-Nitro-2-acetaminobenzoic Acid.*—The ammonium salt was prepared by dissolving the acid in dilute ammonia water and evaporating slowly on a water-bath. The dark-colored residue was then heated in a paraffin-bath until all effervescence had ceased. The mass thus obtained was nearly black. It was extracted with dilute caustic potash, the solution precipitated with carbon dioxide and the precipitate purified as above, giving fine needles, melting with decomposition at 277°-279° (corr.).

(3) *From Nitro-acetylanthranil and Ammonia.*—The anthranil was shaken with a moderate excess of dilute ammonia (1 : 2) until dissolved. On acidifying the solution with acetic acid the quinazoline separated, and without filtering out the precipitate the entire mixture was evaporated to dryness, and the residue recrystallized from a large amount of boiling water. Or, the following process was adopted. The first crop of quinazoline crystals was filtered out, and the filtrate concentrated for a second crop. The mother-liquor from the second crop was evaporated to dryness, heated to 220° as long as any water was given off, and the melt, combined with the second crop crystals, recrystallized from hot water. The object of the heating to 220° was the removal of any water which might have been taken up by the hy-

drolysis of some of the anthranil, *i. e.*, to change the ammonium salt of any nitro-acetylanthranilic acid to the quinazoline. The yield of pure quinazoline obtained from the anthranil was nearly quantitative.

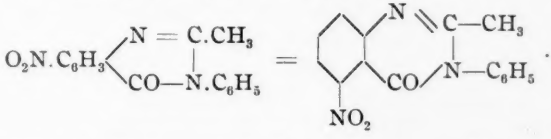
Properties of 5-Nitro-2-methyl-4-ketodihydroquinazoline.—The products obtained by the above three methods were identical in all respects. The pure quinazoline crystallizes from alcohol in fine colorless needles, melting with decomposition at 277°-279° (corr.). It is slightly soluble in hot water, more readily in warm acetone or alcohol, practically insoluble in cold water, hot or cold chloroform, ether, benzene, or petroleum ether. It dissolves readily in dilute alkalies, and is reprecipitated from such solutions by carbon dioxide. Boiling with concentrated caustic potash liberates no ammonia from it. We have not observed any dimorphism in the crystals.

Calculated for $C_9H_7O_3N_3$: C, 52.7; H, 3.4; N, 20.5. Found: C, 52.6, 52.6; H, 3.8, 3.6; N, 20.3.

Chloride.—On treating the quinazoline with concentrated hydrochloric acid the fine needles were changed to a white, amorphous powder, practically insoluble in the acid. All attempts to crystallize it from dilute acid gave only the characteristic crystals of the free quinazoline. The white, amorphous powder melted with decomposition at 276°-279°.

Nitrate.—The quinazoline dissolves with ease in warm dilute nitric acid (1 : 2), and, on cooling, warty masses of needle-like crystals separate. On recrystallization from water needles are obtained which begin to decompose at 205°, but do not melt completely below 260°.

5-Nitro-2-methyl-3-phenyl-4-ketodihydroquinazoline,



—Nitro-acetylanthranil was boiled with excess of aniline, the solution cooled, poured into water, acidified with acetic acid, and the mixture boiled for a few minutes. The quinazoline remained undissolved as a pale brown powder, which was filtered out, and crystallized from a large volume of boiling absolute alcohol.

It is thus obtained in compact cubes, m. p. 233°-234° (corr.), slightly soluble in cold acetone, warm benzene or amyl acetate, easily soluble in warm acetone or boiling nitro-benzene.

Calculated for $C_{15}H_{11}O_3N_3$: C, 64; H, 3.9; N, 14.9. Found: C, 64, 64.1; H, 3.9, 4; N, 14.7.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
March, 1905.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE CHEMISTRY OF FLESH.

(SECOND PAPER.)[1]

IMPROVED METHODS FOR THE ANALYSIS OF ANIMAL SUBSTANCES.[2]

BY H. S. GRINDLEY AND A. D. EMMETT.

Received April 10, 1905.

THE proximate analysis of animal substances is as yet confined to the determination of only a few classes of chemical compounds. In continuing the study of the chemistry of the cooking of meats, upon which considerable work has been done in this laboratory in coöperation with the U. S. Department of Agriculture, Office of Experiment Stations,[3] it became apparent that the ordinary methods used in the analysis of food materials do not give a sufficient amount of information regarding the proximate constituents which uncooked and cooked meats and broths contain, to teach much regarding the nature of the changes resulting in the processes of cooking.

It is also true that the methods of analysis commonly used do not include the direct determination of several constituents of flesh which are of much importance in imparting to meats their characteristic flavors and which in addition possess real value as stimulants to digestion. These principles are the nitrogenous and non-nitrogenous extractives.

Further, there are also serious objections to the customary methods of analysis which require the preliminary preparation of air-dried samples, since this procedure brings about fundamental

[1] First paper: This Journal **26**, 1086 (1904).

[2] This research was made possible through the valuable aid given by the Department of Animal Husbandry of the Agricultural Experiment Station of the University of Illinois.

[3] U. S. Department of Agriculture, Office of Experiment Stations, Bulls. 102 and 104.

changes in the proteid substances and undoubtedly affects, to some extent, the nature of the fats and probably the organic extractives. The changes which the process of air-drying produces in the proteids prevent further separation, determination and examination of these substances, since they are for the most part, if not entirely, made insoluble by this treatment.

In view of these facts it seemed desirable to attempt, in the first place, to analyze directly the fresh substance of meats without first preparing an air-dried sample, which is the usual practice, and in the second place, to prepare and study water extracts of flesh so that, if possible, a more complete differentiation could be made between their proximate principles.

METHOD FOR THE DIRECT ANALYSIS OF FLESH.

As a result of considerable preliminary experimental work it has been demonstrated that the method recommended by the Association of Official Agricultural Chemists may be so modified that it can be used to analyze directly the fresh substance of meats without the previous preparation of air-dried samples. It will, therefore, only be necessary to describe here such modifications as have been found desirable, in order to use the fresh substance of the food materials.

It is essential that much care be taken in preparing and thoroughly mixing the samples for the analysis. In the case of flesh the samples were ground in a sausage mill and the minced meat was then intimately mixed. This operation of grinding and mixing was performed three or four times for each sample. On account of the large proportion of water in the samples of fresh meats all the weighings were made by difference, a glass-stoppered weighing-bottle being used.

For the determination of water the samples were weighed in glass tubes with filter-paper bottoms, such as are ordinarily used in ether extraction of fat by the Hopkins method.[1] In cases where the meat was rather fat, filter blocks, made of Schleicher & Schüll fat-free paper, were first put into the tubes. The tube and contents were dried very slowly at first in the water-oven at a low temperature. The determination was then continued as usual.

The fat was then determined by extracting the dried samples from the estimation of water with anhydrous ether. After twenty-four hours' extraction the samples were removed and intimately

[1] Ill. Agr. Expt. Sta., Bull. **53**, 147 (1898).

ground with ignited sand, then transferred to the moisture tubes again, which were loosely plugged with fat-free cotton to prevent any of the material from being mechanically carried into the flasks. The extraction was then further continued for twelve hours.

The usual Kjeldahl method was used for the determination of the total nitrogen, special care being taken in transferring the weighed meat to the Kjeldahl flask, so that none of the material adhered to the neck of the flask. In the distillation it was found that ignited pumice stone was preferable to granulated zinc. Experiments made in this laboratory show that zinc reduces some form of nitrogen compounds which is usually present in the ordinary alkali and thus introduces a slight error.

The ash was determined as usual, but much care was taken to heat the muffle very slowly and gradually, to begin with, so as to prevent loss by sputtering. The total phosphorus in the meat was determined by the method described by Neumann.[1]

In order to test the accuracy of this method a piece of raw, lean, beef sirloin was thoroughly ground and mixed and then divided into two samples, which were given different laboratory numbers. One of these samples was analyzed completely and carefully by one analyst and the other sample was analyzed by another analyst.

It was not known by either of the analysts that the samples were the same. In the earlier work in testing the methods as to accuracy each determination was made in double duplicates. The results of this test of the method are given below.

TABLE I.—RESULTS OF THE ANALYSIS OF THE SAME SAMPLE BY DIFFERENT ANALYSTS.

Laboratory. No.	Kind of meat.	Water. Per cent.	Protein ($N \times 6.25$) Per cent.	Fat. Per cent.	Ash Per cent.	Total nitrogen. Per cent.
1649*a*	Beef sirloin, raw	75.32	21.50	3.27	1.02	3.44
1649*b*	"	75.53	20.81	2.70	1.03	3.33
1649*c*	"	75.66	21.13	3.07	1.02	3.38
1649*d*	"	75.32	21.62	3.27	0.99	3.46
	Average	75.46	21.27	3.08	1.02	3.40
1650*a*	Beef sirloin, raw	75.81	21.25	3.04	1.02	3.40
1650*b*	"	75.44	21.31	2.99	0.99	3.41
1650*c*	"	75.50	21.31	2.72	1.00	3.45
1650*d*	"	....[1]	21.56	...[2]	1.02	3.41
	Average	75.58	21.36	2.92	1.01	3.42

[1] Dubois Reymond's Archiv. (Physiol. Abth.), 1897, p. 552.

[2] Determination lost.

These figures indicate very clearly that this method, even when used by different analysts, gives concordant results that are strictly comparable with each other.

However, before accepting this method for use in place of the usual method in which the meats were first air-dried, a comparative test was made of the two methods upon a considerable number of samples. For this purpose each cut of meat was very thoroughly sampled and then divided into two portions—one for the direct analysis in which the fresh sample was used as indicated above, and another for the preparation of an air-dried sample which was then analyzed by the usual method. The results of these comparative analyses are given in Table II. The results for each sample of meat are the average of either triplicate or quadruple determinations.

The examination of the data given in the above table leads to the conclusion that while the agreement of the results is not yet as good as would be desired, they are in sufficiently close agreement to fully justify the use of the modified method, in which the food material is analyzed directly without previous air-drying.

In view of the comparative results thus obtained this method of direct analysis has been used exclusively in this laboratory during the last year in the analysis of a large number of samples of raw and cooked meats.

PREPARATION AND ANALYSIS OF COLD WATER EXTRACTS OF FLESH.

Investigations which have been made in this laboratory led to the conclusion that one of the best means of increasing the present very incomplete knowledge of the chemistry of flesh would be a thorough study of the cold water extracts of the fresh substance of the same.

In the past, comparatively little work has been undertaken in this direction, and as far as the writers have been able to discover, no method has been as yet proposed or described for so complete an examination of the cold water extracts of flesh as the one which is given in this paper. After much preliminary experimentation, which it is not necessary to describe in this connection, the following method for the preparation and analysis of the cold water extracts of meats was elaborated and adopted in this laboratory for use in an extended investigation upon the chemistry of flesh.

TABLE II.—COMPARATIVE RESULTS OF THE DIRECT AND AIR-DRIED ANALYSES.

Laboratory No.	Kind of meat.	Results of direct analyses. Water. Per cent.	Protein (N × 6.25). Per cent.	Fat. Per cent.	Ash. Per cent.	Total. Per cent.	Total nitrogen. Per cent.	Results of air-dried analyses. Water. Per cent.	Protein (N × 6.25). Per cent.	Fat. Per cent.	Ash. Per cent.	Total. Per cent.	Total nitrogen. Per cent.
1643	Beef, round, boiled.....	60.52	33.58	5.66	0.74	100.50	5.37	60.57	33.89	5.49	0.64	100.59	5.42
1647	Beef, round, raw.....	74.18	20.96	4.28	1.28	100.70	3.35	73.76	20.73	4.52	1.07	100.08	3.32
1650	Beef, sirloin, raw.....	75.46	21.27	3.08	1.02	100.95	3.40	74.96	21.06	3.06	1.10	100.18	3.37
1656	Veal, leg, raw.....	75.97	21.47	0.96	1.15	99.55	3.47	75.92	21.75	0.88	1.12	99.67	3.48
1665	Beef, neck, boiled.....	54.40	31.49	13.68	0.47	100.04	5.04	55.44	31.28	13.13	0.47	100.32	5.00
1652	Veal, leg, boiled.....	64.73	33.53	1.59	1.01	100.86	5.31	63.79	33.37	1.53	0.97	99.66	5.34
1674	Beef, rump, pan-broiled...	27.46	23.66	47.39	1.18	99.69	3.79	27.44	23.54	47.50	1.15	99.63	3.77
1676	Beef, rump, raw.....	52.26	15.00	32.38	0.74	100.38	2.40	52.38	14.66	32.47	0.71	100.22	2.34
1692	Beef, round, raw.....	76.22	20.93	2.36	1.08	100.59	3.35	76.40	20.41	2.27	1.04	100.12	3.27
1704	Beef, rump, boiled.....	55.01	28.64	16.07	0.68	100.40	4.58	55.05	28.55	15.94	0.70	100.24	4.57
	Average.....	61.62	25.05	12.75	0.94	100.37	4.01	61.57	24.93	12.70	0.90	100.07	3.99
	Maximum difference	+.97	+.52	+.55	+.21	+1.20	+.08	.....	.....	.....	....	.....	....
	Minimum difference	+.02	+.09	+.02	0.00	+.06	—.01	.....	.....	.....	....	.....	....
	Average difference ...	+.05	+.12	+.05	+.04	+.30	+.02	.....	.....	.....	....	.....	....

Preparation of the Cold Water Extracts.—Three portions of 30 to 35 grams each of the thoroughly sampled meat were taken. The weighings were made by difference, a glass-stoppered weighing-tube being used. The meat was thoroughly mixed each time before taking any of it. Each lot of 30 to 33 grams was divided as equally as possible between six small beakers. The samples were moistened with a little distilled water and all the lumps completely broken up with a glass rod. Fifty cc. of water were then added to each beaker and the contents stirred thoroughly for fifteen minutes. After allowing three to five minutes for the insoluble residue to settle, the liquid for each beaker was decanted through filters into 250-cc. flasks. The insoluble portion was thoroughly drained and then 25 cc. of water were added. The water and residue were thoroughly stirred for seven to eight minutes and after settling decanted upon the same filter. This treatment was continued—using each time 25 cc. of water—until the filtrate measured about 230 cc. The filters were allowed to drain completely between each extraction. After the last extraction the entire contents of each beaker were thrown upon the filter and, when drained, washed twice with a small quantity of distilled water. The filtrates were then made up to 5 liters, after rinsing each flask twice with water.

Completion of the Extraction with Cold Water.—In order to test whether or not the extraction with cold water, as made above, was complete, a second extract of the residues of meat from the first extraction was prepared. This second extraction was made exactly like the first one in every detail. The second cold water extract was diluted to the same volume as the first and it was also analyzed by exactly the same methods.

Further, a third extract was also prepared from a portion of the insoluble residues left from the second extraction, in which only the total solids and ash were determined.

In order to further check the accuracy of the methods for the preparation and analysis of the water extracts of meats, after the second extraction with cold water, a portion of the insoluble residues was used for the determination of total nitrogen, fat and ash. The results of these several experiments are tabulated in the following table.

TABLE III.—RESULTS SHOWING COMPLETION OF EXTRACTION WITH COLD WATER.

Constituents.	Raw meat before extraction. Lab. No. 1737. Per cent.	Cold water extracts. First extraction. Lab. No. 1737. Per cent.	Second extraction. Lab. No. 1738. Per cent.	Third extraction. Lab. No. 1740. Per cent.	Insoluble residue from second extraction. Lab. No. 1739. Per cent.	Sum of residue and first and second extractions. Per cent.
Total solids	.....	7.0280	0.1110	0.0910	.....	.....
Total ash	1.19	0.8513	none	none	0.1400	1.0913
Total nitrogen	3.609	0.8435	0.0148	0.0069	2.7410	3.5993
Nitrogen coagulated by heat	.....	0.3925	0.0040	.....	.....	.....
Nitrogen precipitated by $ZnSO_4$	.....	0.0473	0.0082	.....	.....	.....
Sum of coagulable and albumose nitrogen	.....	0.4398	0.0122	.....	.....	.....
Nitrogen precipitated by tannin and salt	.....	0.4331	0.0071	.....	.....	.....
Non-proteid nitrogen	.....	0.4037	0.0026	.....	.....	.....
Total fat	2.78	.....	.....	.....	2.53	2.53
Water	73.23	.....	.....	.....	.....	.....

These results indicate that the method used in preparing the cold water extracts does not give entirely complete extraction. The total solids in the second water extract amounted to only 1.58 per cent. of the total solids in the first cold water extract. The total nitrogen of the second extraction equaled only 0.41 per cent. of the total quantity of nitrogen existing in the first extract. Considering the difficulties attending this work, it seems to the writers that the extraction can be considered practically complete and that the results are quite within the limits of error.

ANALYSIS OF COLD WATER EXTRACTS.

Determination of Total Solids and Ash.—Portions of 100 cc. each of the cold water extract were evaporated to dryness in weighed platinum dishes. The residues were dried in the water-oven for periods of one hour until the weight of each was approximately constant. The dried residues were ignited carefully over the free flame at a low red heat until colorless or nearly so. The ash was weighed quickly, reheated and weighed again. The treatment was repeated until the weight was constant.

Determination of Total Nitrogen.—Portions of 100 cc. each of the extract were used to determine the nitrogen by the usual Kjeldahl method. Dilute standard solutions, about N/15, were used for this part of the work.

Coagulable Proteids.—To begin with, considerable trouble was experienced in this determination in getting even fairly concordant results. It has been found in this work that even a very slight excess of acetic acid interferes materially with the complete separation and proper coagulation of the coagulable proteids occurring in water solutions of raw meats. Professor W. O. Atwater,[1] in the study of the chemical composition of fish, found that the presence of acetic acid instead of increasing the amount of proteid coagulated in a water solution of fresh fish, was very apt to hinder coagulation and sometimes prevent it altogether. In this laboratory it has been found that in the presence of acetic acid the proteid separates as a slimy film upon the surface of the liquid, the coagulation being incomplete and the filtration taking place very slowly. In all cases an additional separation takes place upon further evaporation of the filtrate for the precipitation of albumoses and also upon neutralization. In fact, separation of additional proteid continues until the solution is evaporated to dryness upon the water-bath. This incomplete coagulation resulted even when 2 cc. of N/10 acetic acid was used. Such difficulties were not so apparent in the analysis of cold water extracts from cooked meats, which, however, contained as a rule very slight amounts of coagulable proteids.

In order to overcome these difficulties the coagulation in the latter determinations was brought about in a neutral solution, after some preliminary experiments had proved conclusively that under such conditions the precipitation of coagulable matter was more complete, that the filtration under such conditions always took place readily, and that more concordant results were obtained. It was also proved that the coagulation was more complete when the solutions were made neutral to litmus paper, than it was when the solutions were made neutral to phenolphthalein. In order to test the influence of acids and alkalies upon the coagulation of the proteids contained in the cold water extracts of flesh the following experiment was made: Fifteen portions of a cold water extract of meat, measuring 200 cc. each, were taken.

[1] U. S. Fish Commissioner's Report for 1880, p. 244 (Washington, 1883).

Three of these portions were each treated with 2 cc. of N/10 acetic acid. They were all then carefully evaporated upon the water-bath until the volume in each case was reduced to 50 cc. The twelve portions to which no acetic acid had been added coagulated very nicely, while the three fractions which contained acetic acid failed to coagulate, but a slimy film separated upon the surface of the liquids.

After the volume of the solutions had been reduced to 50 cc. the beakers containing the liquids were removed from the water-bath and treated as follows:

(*a*) Three portions were exactly neutralized with N/10 NaOH solution, using litmus as indicator. For this purpose 0.35 cc. of N/10 NaOH solution were required.

(*b*) Three portions were each treated with 0.70 cc. NaOH solution, which made them slightly, but distinctly alkaline to litmus paper.

(*c*) Three portions were exactly neutralized with N/10 NaOH solution, using phenolphthalein as indicator. These solutions required 4.4 cc. of N/10 NaOH solution.

(*d*) Three portions were each treated with 2 cc. of N/10 acetic acid solution.

(*e*) The three portions containing the 2 cc. of acetic acid were not neutralized or changed in any way.

After the above treatments the fifteen portions were all replaced upon the water-bath for fifteen minutes and then filtered immediately while hot. The resulting coagulated precipitates were thoroughly washed with boiling water and the nitrogen determined in them by the Kjeldahl method. The filtrates and washings were all replaced upon the water-bath and then concentrated to 50 cc. No additional precipitates were formed. All solutions were now made exactly neutral to litmus and evaporated to 25 cc. In (*a*) where the solutions were made neutral to litmus by adding 0.35 cc. of N/10 NaOH solution, and in (*b*) where the solutions were made only slightly alkaline to litmus by the addition of 0.70 cc. of N/10 NaOH solution there were no additional precipitates formed by this treatment. In (*e*) where 2 cc. of acetic acid were added before evaporation, in (*c*) where the solutions were neutralized with N/10 NaOH solution, using phenolphthalein as indicator, and in (*d*) where the solutions were treated with 2 cc. of N/10 acetic acid after evaporation, there were additional

precipitates produced upon neutralization and evaporation. These were separated and washed as above and then the nitrogen determined.

The complete results of these experiments are given in the table on the following page.

These preliminary experiments, together with others which confirmed these results, led to the adoption of the following method for the determination of the coagulable proteids in cold water extracts of flesh: Portions measuring 200 cc. each were evaporated upon the water-bath to a volume of 50 cc. The solutions were then exactly neutralized with N/10 NaOH solution, litmus paper being used as the indicator. The neutral solutions were warmed upon the water-bath for ten minutes and immediately filtered and the coagulated residues washed thoroughly with hot water. The nitrogen in the residue was determined, much care being taken to remove all the coagulated proteid from the beakers by the aid of hot concentrated sulphuric acid.

Albumoses and Proteoses.—For the determination of these substances in the water extracts of meats, the zinc sulphate method proposed by A. Bömer[1] was used. Special precautions were taken in order to have the conditions of precipitation the same as regards temperature, acidity, volume of liquid and time of standing. The details of the method of procedure finally decided upon were as follows: The filtrates and washings from the above determinations of coagulable proteid, after slight acidification with acetic acid, were evaporated upon the water-bath to a volume of 30 cc. and allowed to cool. One cc. of 50 per cent. sulphuric acid was added and the solution completely saturated with crystallized zinc sulphate. The solution was then heated upon the water-bath with constant stirring until perfectly clear, allowed to stand twelve hours, filtered, and the precipitate thoroughly washed with a completely saturated solution of zinc sulphate, slightly acidified with sulphuric acid. The nitrogen in the precipitate was determined by the Kjeldahl method.

Peptones.—Tannic acid has long been recognized as an excellent precipitant for proteid bodies. Almen[2] probably first used tannin as a quantitative reagent for proteids. The following investigators have made use of this reagent for the estimation and separa-

[1] *Z. anal. Chem.*, **34**, 562 (1895).

[2] Upsala lakareforenings forhandlingor (1870).

TABLE IV.—INFLUENCE OF ACIDITY AND ALKALINITY UPON COAGULATION OF PROTEIDS.

Method of procedure : First experiment.	First test. Per cent.	Second test. Per cent.	Third test. Per cent.	Average. Per cent.
(*a*) Neutralized with 0.35 cc. of NaOH (litmus)	0.4040	0.4033	0.4038	0.4037
(*b*) Made slightly alkaline with 0.7 cc. of NaOH (litmus)	0.4054	0.4049	0.4049	0.4059
(*c*) Neutralized with 4.4 cc. of NaOH (phenolphthalein), first precipitate	0.3984	0.3855	0.3989	0.3943
" " " " " " second precipitate	0.0085	0.0096	0.0096	0.0092
" " " " " " total	0.4069	0.3951	0.4085	0.4035
(*d*) Acidified with 2 cc. of acid, after evaporation, first precipitate	0.4019	0.3980	0.3924	0.3974
" " " " " " second precipitate	0.0078	0.0051	0.0085	0.0071
" " " " " " total	0.4097	0.4031	0.4009	0.4046
(*e*) Acidified with 2.0 cc. of acid before evaporation, first precipitate	0.1237	0.2296	0.2333	0.1955
" " " " " " " second precipitate	0.2763	0.1913	0.1665	0.2114
" " " " " " " total	0.4000	0.4209	0.3998	0.4069
Method of procedure : Second experiment.				
(*a*) Neutralized with 0.25 cc. of NaOH (litmus)	0.4620	0.4565	0.4639	0.4608
(*b*) Made slightly alkaline with 0.5 cc. of NaOH (litmus)	0.4651	0.4636	0.4623	0.4637
(*c*) Neutralized with 3.9 cc. of NaOH (phenolphthalein) first precipitate	0.4562	0.4484	0.4574	0.4540
" " " " " " " second precipitate	0.0110	0.0091	0.0090	0.0097
" " " " " " " total	0.4672	0.4575	0.4664	0.4637
(*d*) Acidified with 2.0 cc. of acid before evaporation, first precipitate	0.1526	0.0670	0.1469	0.1222
" " " " " " " second precipitate	0.3068	0.3869	0.3136	0.3357
" " " " " " " total	0.4594	0.4539	0.4605	0.4579

tion of proteid nitrogen from non-proteid nitrogen in the various organic substances which they have studied: Libarius, Girgensohn, Taraszewicz, Sebelien, Mallet, Vivian, Schjerning, Van Slyke and Hart, Bigelow and others. It is still a disputed question as to whether tannin is a complete precipitant for all kinds of proteids, but the literature regarding this matter is too comprehensive to take up in connection with this paper. Tannin and salt have been used in this research for two purposes, first to determine the quantity of peptones, if present, and second, since peptones occur in very small quantity, if at all, in fresh flesh, the results which have been obtained by this precipitant have been used as a check upon the total soluble proteid nitrogen which was obtained by the summation of the nitrogen precipitated by coagulation and by zinc sulphate.

In the first part of this work tannin and sodium chloride were used as a precipitant under the following conditions: Portions of the cold water extracts of raw and cooked meats measuring 200 cc. were transferred into 250-cc. measuring flasks and then treated directly with 1 gram of sodium chloride and 5 cc. of a solution containing 12 per cent. of tannic acid. The solution was then diluted to 250 cc., allowed to stand twelve hours or more, filtered through a dry filter and the nitrogen determined in a measured volume of 200 cc. of the filtrate.

In later work, tannin and salt have been used not directly upon the cold water extracts, but upon the filtrates resulting from the coagulation of the proteids in neutral solutions. In such cases the details of the procedure were as follows: Portions of the cold water extracts of raw and cooked meats measuring 200 cc. were carefully evaporated upon the water-bath until the volume in each case was reduced to 50 cc. The liquids were then exactly neutralized with N/10 NaOH solution, using litmus paper as an indicator, and they were then replaced upon the water-bath for fifteen minutes. The coagulable proteid was then removed immediately by filtration and thoroughly washed with hot water. The filtrates and washings were replaced upon the water-bath, concentrated to about 75 cc. and then transferred to 110-cc. measuring flasks. One gram of salt dissolved in 5 cc. of water and 5 cc. of tannic acid were added. The solution was then diluted to a volume of 110 cc., thoroughly mixed and allowed to stand

over night. The solutions were filtered through dry filters and the nitrogen determined in 100-cc. portions of the filtrates.

The amount of nitrogen in the form of peptones was determined by difference; that is, by subtracting from the nitrogen precipitated by tannin and salt, the combined amount of nitrogen precipitated by coagulation and by zinc sulphate.

Inorganic and Organic Phosphorus.—The total soluble phosphorus was determined in 250-cc. portions of the cold water extract by the Neumann method. The inorganic phosphorus in the cold water extracts of meats was determined in 500-cc. portions of the solution by the method finally adopted by Hart and Andrews[1] with such modifications as it has been found necessary to make in the case of meats. The method now used for the work in this laboratory is as follows: The 500-cc. portions are evaporated to about 100 cc. and filtered to remove the coagulated proteid. The filtrates are made neutral to litmus paper by ammonium hydroxide and about 8 grams of ammonium nitrate added to the same. The solutions are then warmed to 60° C., and 3 cc. of nitric acid (sp. gr. 1.20) are added. The inorganic phosphorus is then precipitated by an excess of a clear, neutral solution of ammonium molybdate. After the addition of the precipitant the solution is digested for fifteen minutes at a temperature of 60° C., and then allowed to stand at the temperature of the laboratory for two hours. After filtration, the precipitate is dissolved in ammonium hydroxide and then reprecipitated by acid ammonium molybdate and the determination continued as usual. The phosphorus thus precipitated was considered to be that due to inorganic phosphates.

In connection with the study of the cold water extracts of flesh a somewhat extended research was made to determine the relative value of the following reagents for the separation and estimation of proteid and non-proteid nitrogen: Phosphotungstic acid in the cold, phosphotungstic acid in the hot, bromine, and Stützer's reagent. The results of this work will be published in a later paper.

Calculation of the Final Results of Analysis.—By the direct analysis of the fresh meats the following data are obtained: The percentage of water, total nitrogen, fat, ash and total phosphorus. From the results of the analysis of the cold water extract of the

[1] *Am. Chem. J.*, 30, 470.

meats the following data are directly obtained: The percentage of soluble ash, soluble nitrogen, soluble nitrogen coagulable by heat, albumose nitrogen, peptone nitrogen, total soluble phosphorus, soluble inorganic phosphorus and total soluble matter.

From the two sets of analytical data mentioned above which are obtained by direct determination, it is possible to represent the composition of the flesh in the following terms: Soluble coagulable proteid, albumose, peptone, total soluble proteid, insoluble proteid, total proteid, nitrogenous extractives, non-nitrogenous extractives, total organic extractives, fat, soluble ash, insoluble ash, total ash, soluble inorganic phosphorus, soluble organic phosphorus, total soluble phosphorus, insoluble phosphorus and total phosphorus.

The soluble coagulable proteid, albumose and peptone are obtained by multiplying the nitrogen existing in these forms by the factor 6.25. The total soluble proteid is equivalent to the sum of these last three quantities. The insoluble proteid is obtained by subtracting the total soluble nitrogen from the total nitrogen in the meat and then multiplying this difference by the factor 6.25. The total proteid is obtained by the summation of the soluble and the insoluble proteid.

The percentage of the nitrogenous organic extractives is calculated by subtracting the soluble proteid nitrogen from the total soluble nitrogen and then multiplying this difference by the factor 3.12. The non-nitrogenous extractives are found by subtracting the sum of the total soluble proteid, the nitrogenous extractives and the soluble ash from the total soluble material found by direct determination. The total organic extractives represent the sum of the nitrogenous and non-nitrogenous extractives.

The fat and total ash are determined directly in the fresh substance of the flesh. The soluble ash is found directly in the cold water extract. The insoluble ash is obtained by difference.

The total phosphorus, the total soluble phosphorus and the soluble inorganic phosphorus are determined as indicated above. The soluble organic phosphorus and the insoluble phosphorus are obtained by difference.

The representative results given in the following tables indicate the extent and character of the information furnished by use of the improved methods of analysis herewith reported, as compared with the results obtained by the ordinary method of analysis.

TABLE V.—CHEMICAL COMPOSITION OF MEATS BY THE IMPROVED METHODS OF ANALYSIS—FRESH SUBSTANCE.

Laboratory No.	Kind of meat.	Dry substance. Water. Per cent.	Dry substance. Soluble. Per cent.	Dry substance. Insoluble. Per cent.	Dry substance. Total. Per cent.	Proteid. Soluble. Coagulable. Per cent.	Proteid. Soluble. Albumose. Per cent.	Proteid. Soluble. Peptones. Per cent.	Proteid. Soluble. Total. Per cent.	Proteid. Insoluble. Per cent.	Proteid. Total. Per cent.	Organic extractives. Nitrogenous. Per cent.	Organic extractives. Non-nitrogenous. Per cent.	Organic extractives. Total. Per cent.	Fat. Per cent.
1850	Beef, round, raw	74.89	7.26	18.00	25.26	2 62	0.23	0.08	2.93	15.67	18.60	1.34	2.00	3 34	2.24
1823	Beef, round, raw	75.61	6.21	18.19	24.40	2.08	0.23	0.10	2.41	15.97	18.38	1.26	1.54	2.80	2.14
1857	Veal, breast, raw	63.34	4.65	31.86	36.51	1.55	0.18	0.06	1.79	15.10	16.89	0.78	1.42	2.20	16.52
1860	Veal, leg, raw	73 40	5.81	21.50	27.31	1.52	0.22	0.10	1.84	16.28	18.12	1.21	1.87	3.08	5.02
1831	Beef, ribs, roast	44.78	2.76	52.32	55.08	0.36	c.14	0.02	0.52	15.30	15.82	0.77	0.82	1.59	36.84
1838	Beef, ribs, roast	49.73	3.04	47.63	50.67	0.26	0.12	0.00	0.38	19.65	20.03	0.91	1.04	1.95	27.79
1829	Beef, round, pot-roast	57.57	3.24	39.61	42.85	0.00	0.43	0.03	0.46	35.14	35.60	1.01	1.09	2.10	4.20
1825	Beef, round, pot-roast	56.92	4.24	40.11	44.35	0.00	0.32	0.05	0.37	34.32	34.69	1.31	1.53	2.84	5.58
1824	Beef, round, boiled	55.96	2.92	41.69	44.61	0.00	0.39	0.02	0.41	33.01	33.42	0.83	1.06	1.89	8.47
1808	Beef, round, boiled	61.70	1.76	37.24	39.00	0.00	0.19	0.14	0.33	33.45	33.78	0.47	0.54	1.01	3.65

Laboratory No.	Kind of meat.	Ash. Soluble. Per cent.	Ash. Insoluble. Per cent.	Ash. Total. Per cent.	Nitrogen. Soluble. Proteid. Per cent.	Nitrogen. Soluble. Non-proteid. Per cent.	Nitrogen. Soluble. Total. Per cent.	Nitrogen. Insoluble. Per cent.	Nitrogen. Total. Per cent.	Nitrogen. Ratio of non-proteid to proteid. In water extracts. Ratio.	Nitrogen. Ratio of non-proteid to proteid. In meats. Ratio	Phosphorus. Soluble. Inorganic. Per cent.	Phosphorus. Soluble. Organic. Per cent.	Phosphorus. Soluble. Total. Per cent.	Phosphorus. Insoluble. Per cent.	Phosphorus. Total. Per cent.
1850	Beef, round, raw	0.99	0.09	1.08	0.469	0.431	0.900	2.506	3.406	1 : 1.09	1 : 7.91	0.153	0.104	0.257	0.088	0.345
1823	Beef, round, raw	1.00	0.08	1.08	0.386	0.402	0.788	2.556	3.344	1 : 0.96	1 : 8.42	0.090	0.097	0.187	0.035	0.222
1857	Veal, breast, raw	0.66	0.24	0.90	0.286	0.251	0.537	2 416	2.953	1 : 1.14	1 : 11.76	0.075	0.037	0.112	0.087	0.199
1860	Veal, leg, raw	0.89	0.20	1.09	0 292	0.387	0.679	2.605	3.284	1 : 0.75	1 : 8.49	0.118	0.039	0.157	0.064	0.221
1831	Beef, ribs, roast	0.65	0.18	0.83	0.082	0.248	0.330	2.449	2.779	1 : 0.33	1 : 11.21	0.095	0.023	0.118	0.030	0.148
1838	Beef, ribs, roast	0.71	0.19	0.90	0.060	0.292	0.352	3.144	3.496	1 : 0.21	1 : 11.97	0.104	0.044	0.148	0.042	0 190
1829	Beef, round, pot-roast	0.68	0.27	0.95	0.073	0.322	0.395	5.623	6.018	1 : 0.23	1 : 18.70	0.112	0.049	0.161	0.066	0.227
1825	Beef, round, pot-roast	1.03	0.21	1.24	0.059	0.419	0.478	5 491	5.969	1 : 0.14	1 : 14.24	0.122	0 059	0.181	0.083	0.264
1824	Beef, round, boiled	0.62	0.21	0.83	0.039	0 266	0.305	5.306	5.611	1 : 0.15	1 : 21.10	0.085	0 041	0.126	0.087	0.213
1808	Beef, round, boiled	0.42	0.14	0.56	0.053	0.151	0.204	5.351	5.555	1 : 0.35	1 : 36.79	. .	. .	0.068	0.094	0.162

TABLE VI.—CHEMICAL COMPOSITION OF MEATS BY THE ORDINARY METHOD OF ANALYSIS—FRESH SUBSTANCE.

Laboratory No.	Kind of meat.	Water. Per cent.	Dry substance. Per cent.	Proteid (N × 6.25). Per cent.	Fat. Per cent.	Ash. Per cent.	Total nitrogen. Per cent.
1850	Beef, round, raw.....	74.89	24.61	21.29	2.24	1.08	3.406
1823	Beef, round, raw.....	75.61	24.13	20.91	2.14	1.08	3.345
1857	Veal, breast, raw.....	63.34	35.88	18.46	16.52	0.90	2.953
1860	Veal, leg, raw.....	73.40	26.64	20.53	5.02	1.09	3.284
1831	Beef, ribs, roast.....	44.78	55.04	17.37	36.84	0.83	2.779
1838	Beef, ribs, roast.....	49.73	50.54	21.85	27.79	0.90	3.496
1829	Beef, round, pot-roast...	57.57	42.76	37.61	4.20	0.95	6.018
1825	Beef, round, pot-roast...	56.92	44.13	37.31	5.58	1.24	5.969
1824	Beef, round, boiled.....	55.96	44.37	35.07	8.47	0.83	5.611
1808	Beef, round, boiled.....	61.70	38.93	34.72	3.65	0.56	5.555

For Table VII see next page.

TABLE VIII.—CHEMICAL COMPOSITION OF MEATS BY THE ORDINARY METHOD OF ANALYSIS—WATER-FREE SUBSTANCE.

Laboratory No.	Kind of meat.	Dry substance. Per cent.	Proteid (N × 6.25). Per cent.	Fat. Per cent.	Ash. Per cent.	Total nitrogen. Per cent.
1850	Beef, round, raw.....	100.00	86.51	9.10	4.39	13.840
1823	Beef, round, raw.....	100.00	86.66	8.87	4.47	13.862
1857	Veal, breast, raw.....	100.00	51.45	46.04	2.51	8.232
1860	Veal, leg, raw.....	100.00	77.07	18.84	4.09	12.327
1831	Beef, ribs, roast.....	100.00	31.56	66.93	1.51	5.049
1838	Beef, ribs, roast.....	100.00	43.23	54.99	1.78	6.917
1829	Beef, round, pot-roast....	100.00	87.96	9.82	2.22	14.074
1825	Beef, round, pot-roast....	100.00	84.55	12.64	2.81	13.526
1824	Beef, round, boiled.....	100.00	79.04	19.09	1.87	12.646
1808	Beef, round, boiled.....	100.00	89.19	9.37	1.44	14.269

TABLE IX.—CHEMICAL COMPOSITION OF MEATS BY THE ORDINARY METHOD OF ANALYSIS—WATER-FREE AND FAT-FREE SUBSTANCE.

Laboratory No.	Kind of meat.	Fat-free dry substance. Per cent.	Proteid. Per cent.	Ash. Per cent.	Total nitrogen. Per cent.
1850	Beef, round, raw.....	100.00	95.17	4.83	15.225
1823	Beef, round, raw.....	100.00	95.09	4.91	15.211
1857	Veal, breast, raw.....	100.00	95.35	4.65	15.256
1860	Veal, leg, raw.....	100.00	95.00	5.00	15.189
1831	Beef, ribs, roast.....	100.00	95.44	4.56	15.269
1838	Beef, ribs, roast.....	100.00	96.05	3.95	15.367
1829	Beef, round, pot-roast....	100.00	97.54	2.46	15.607
1825	Beef, round, pot-roast....	100.00	96.80	3.20	15.488
1824	Beef, round, boiled.....	100.00	97.69	2.31	15.627
1808	Beef, round, boiled.....	100.00	98.42	1.58	15.745

TABLE VII.—CHEMICAL COMPOSITION OF MEATS BY THE IMPROVED METHODS OF ANALYSIS—WATER-FREE SUBSTANCE.

Laboratory No.	Kind of meat.	Dry substance. Soluble. Per cent.	Dry substance. Insoluble. Per cent.	Dry substance. Total. Per cent.	Proteid. Soluble. Coagulable. Per cent.	Proteid. Soluble. Albumose. Per cent.	Proteid. Soluble. Peptones. Per cent.	Proteid. Soluble. Total. Per cent.	Proteid. Insoluble. Per cent.	Proteid. Total. Per cent.	Organic extractives. Nitrogenous. Per cent.	Organic extractives. Non-nitrogenous. Per cent.	Organic extractives. Total. Per cent.
1850	Beef, round, raw	28.74	71.26	100.00	10.37	0.91	0.32	11.60	62.03	73 63	5.30	7.92	13.22
1823	Beef, round, raw	25.45	74.55	100.00	8.53	0.94	0.41	9.88	65.45	75.33	5.16	6.31	11.47
1857	Veal, breast, raw	12.74	87.26	100.00	4.24	0.50	0.16	4.90	41.36	46.26	2.14	3.89	6.03
1860	Veal, leg, raw	21.27	78.73	100.00	5.57	0.81	0.36	6.74	59.61	66.35	4.43	6.86	11.29
1831	Beef, ribs, roast	5.01	94.99	100.00	0.65	0.25	0.04	0.94	27.78	28.72	1.40	1.49	2.89
1838	Beef, ribs, roast	6.00	94.00	100.00	0.51	0.24	0.00	0.75	38.78	39.53	1.80	2.05	3.85
1829	Beef, round, pot-roast	7.56	92.44	100.00	0.00	1.00	0.07	1.07	82.01	83.08	2.36	2.54	4.90
1825	Beef, round, pot-roast	9.56	90.44	100.00	0.00	0.72	0.11	0.83	77.39	78.22	2.95	3.45	6.40
1824	Beef, round, boiled	6.55	93.45	100.00	0.00	0.86	0.04	0.92	74.01	74.91	1.86	2.38	4.24
1808	Beef, round, boiled	4.51	95.49	100.00	0.00	0.49	0.36	0.85	85.77	86.62	1.21	1.38	2.59

Laboratory No.	Kind of meat.	Fat. Per cent.	Ash. Soluble. Per cent.	Ash. Insoluble. Per cent.	Ash. Total. Per cent.	Nitrogen. Soluble. Proteid. Per cent.	Nitrogen. Soluble. Non-proteid. Per cent.	Nitrogen. Soluble. Total. Per cent.	Nitrogen. Insoluble. Per cent.	Nitrogen. Total. Per cent.	Phosphorus. Soluble. Inorganic. Per cent.	Phosphorus. Soluble. Organic. Per cent.	Phosphorus. Soluble. Total. Per cent.	Phosphorus. Insoluble. Per cent.	Phosphorus. Total. Per cent.
1850	Beef, round, raw	8.87	3.92	0.36	4.28	1.857	1.706	3.563	9.920	13.483	0.606	0.412	1.018	0.348	1.366
1823	Beef, round, raw	8.77	4.10	0.32	4.42	1.583	1.647	3.230	10.475	13.705	0.369	0.397	0.766	0.144	0.910
1857	Veal, breast, raw	45.25	1.81	0.66	2.47	0.783	0.687	1.471	6.617	8.088	0.205	0.101	0.306	0.239	0.545
1860	Veal, leg, raw	18.40	3.26	0.73	3.99	1.069	1.417	2.486	9.546	12.032	0.432	0.143	0.575	0.234	0.809
1831	Beef, ribs, roast	66.88	1.18	0.33	1.51	0.150	0.449	0.599	4.446	5.045	0.172	0.042	0.214	0.055	0.269
1838	Beef, ribs, roast	54.85	1.40	0.38	1.78	0.119	0.576	0.695	6.205	6.900	0.205	0.087	0.292	0.083	0.375
1829	Beef, round, pot roast	9.80	1.58	0.64	2.22	0.171	0.752	0.923	13.121	14.044	0.262	0.114	0.376	0.154	0.530
1825	Beef, round, pot-roast	12.58	2.32	0.47	2.79	0.134	0.945	1.079	12.380	13.459	0.275	0.133	0.408	0.187	0.595
1824	Beef, round, boiled	18.99	1.39	0.47	1.86	0.088	0.596	0.684	11.894	12.578	0.191	0.092	0.283	0.195	0.478
1808	Beef, round, boiled	9.36	1.08	0.36	1.44	0.137	0.386	0.523	13.721	14.244	. .	. .	0.174	0.241	0.415

TABLE X.—CHEMICAL COMPOSISION OF MEATS BY THE IMPROVED METHODS OF ANALYSIS WATER-FREE AND FAT-FREE SUBSTANCE.

Laboratory No.	Kind of meat.	Fat-free dry substance. Soluble. Per cent.	Fat-free dry substance. Insoluble. Per cent.	Fat-free dry substance. Total. Per cent.	Proteid. Soluble. Coagulable. Per cent.	Proteid. Soluble. Albumose. Per cent.	Proteid. Soluble. Peptones. Per cent.	Proteid. Soluble. Total. Per cent.	Proteid. Insoluble. Per cent.	Proteid. Total. Per cent.	Organic extractives. Nitrogenous. Per cent.	Organic extractives. Non-nitrogenous. Per cent.	Organic extractives. Total. Per cent.
1850	Beef, round, raw	31.54	68.46	100.00	11.38	1.00	0.35	12.73	68.07	80.80	5.82	8.69	14.51
1823	Beef, round, raw	27.90	72.10	100.00	9.35	1.03	0.45	10.83	71.74	82.57	5.65	6.92	12.57
1857	Veal, breast, raw	23.27	76.73	100.00	7.75	0.91	0.29	8.95	75.54	84.49	3.91	7.10	11.01
1860	Veal, leg, raw	26.10	73.91	100.00	6.83	0.99	0.44	8.26	73.05	81.31	5.43	8.41	13.84
1831	Beef, ribs, roast	15.13	84.87	100.00	1.96	0.75	0.12	2.83	83.88	86.71	4.23	4.50	8.73
1838	Beef, ribs, roast	13.29	86.71	100.00	1.13	0.53	0.00	1.66	85.89	87.55	3.99	4.54	8.53
1829	Beef, round, pot-roast	8.38	91.62	100.00	0.00	1.11	0.08	1.19	90.92	92.11	2.62	2.81	5.43
1825	Beef, round, pot-roast	10.94	89.06	100.00	0.00	0.82	0.13	0.95	88.53	89.48	3.37	3.95	7.32
1824	Beef, round, boiled	8.09	91.91	100.00	0.00	1.06	0.05	1.11	91.36	92.47	2.29	2.94	5.23
1808	Beef, round, boiled	4.98	95.02	100.00	0.00	0.54	0.40	0.94	94.63	95.57	1.33	1.52	2.85

Laboratory No.	Kind of meat.	Ash. Soluble. Per cent.	Ash. Insoluble. Per cent.	Ash. Total. Per cent.	Nitrogen. Soluble. Proteid. Per cent.	Nitrogen. Soluble. Non-proteid. Per cent.	Nitrogen. Soluble. Total. Per cent.	Nitrogen. Insoluble. Per cent.	Nitrogen. Total. Per cent.	Phosphorus. Soluble. Inorganic. Per cent.	Phosphorus. Soluble. Organic. Per cent.	Phosphorus. Soluble. Total. Per cent.	Phosphorus. Insoluble. Per cent.	Phosphorus. Total. Per cent.
1850	Beef, round, raw	4.30	0.39	4.69	2 038	1.872	3.910	10.885	14.795	0.665	0.452	1.117	0.382	1.499
1823	Beef, round, raw	4.49	0.35	4.84	1.735	1.805	3.541	11.477	15.020	0.404	0.435	0.839	0.157	0.996
1857	Veal, breast, raw	3.31	1.20	4 51	1.430	1.255	2.687	12.104	14.772	0.374	0.185	0.559	0.436	0.995
1860	Veal, leg, raw	4.00	0.89	4.89	1.308	1.737	3.045	11.700	14.745	0 529	0.175	0.704	0.287	0.991
1831	Beef, ribs, roast	3.56	1.00	4.56	0.453	1.356	1.809	13.424	15 232	0.521	0.126	0.647	0.164	0.811
1838	Beef, ribs, roast	3.10	0.84	3.94	0.264	1.276	1.540	13.743	15.283	0.455	0.192	0.647	0.183	0.830
1829	Beef, round, pot-roast	1.75	0.71	2.46	0.190	0.833	1.023	14.546	15.569	0.290	0.127	0.417	0.170	0.587
1825	Beef, round, pot-roast	2.66	0.54	3.20	0.153	1.081	1.234	14.162	15.498	0.315	0.152	0.467	0.214	0.681
1824	Beef, round, boiled	1.72	0.58	2.30	0.179	0.736	0.915	14 615	15.530	0.235	0.114	0.349	0.241	0.590
1808	Beef, round, boiled	1.19	0.40	1.59	0.151	0.426	0.577	15.138	15.715	. .	. .	0.192	0.266	0.458

DISCUSSION OF RESULTS.

It is quite evident from the analytical data presented in the above tables that the modified method of the chemical analyses gives a much more comprehensive knowledge of the chemical composition of flesh than does the ordinary method of analysis.

In the first place, the improved method of analysis shows that a considerable proportion of the dry substance of either the raw or cooked meats is soluble in cold water. From one-fourth to one-third of the total dry material of lean raw meats is soluble under these conditions, while a smaller proportion of fat meats and cooked meats is soluble.

In the second place, the results obtained by the methods of analysis here suggested demonstrate the fact that the proteids contained in flesh differ in character and properties. A large proportion of the proteid material of raw flesh is insoluble in water, but there is a considerable part of the same soluble in cold water. Of the soluble proteids of raw meat the greater quantity is coagulable by heat. However, in addition to the coagulable proteids the cold water extracts of raw flesh contain albumoses which are precipitated by zinc sulphate, and also, apparently slight amounts of peptones which are not precipitated by coagulation or by saturation with zinc sulphate, but which are precipitated by tannin and salt. It is more than probable, however, that this apparently small quantity of peptones is due to the precipitation of a small part of the nitrogenous extractives by the tannin and salt. The amount and character of the proteids of cooked meats vary with the methods of cooking, but in all cases the percentage of the soluble proteids is less and the percentage of the insoluble proteids is greater than it is in uncooked meats.

In the third place, the data here presented prove that meats contain a considerable quantity of the so-called organic extractives. This method of analysis indicates clearly that these organic extractives are not entirely nitrogenous in nature, but that they contain also non-nitrogenous substances. In fresh, lean beef the percentage of nitrogenous organic extractives varies from 1.00 to 1.75, and the non-nitrogenous organic extractives vary from 1.40 to 2.20. The amount of these organic extractives in cooked meats depends upon the method of cooking.

The usual method of calculating the percentage of proteid in

meats by multiplying the total nitrogen by the factor 6.25, evidently gives a much higher figure for the true proteids than should be assigned to them. For example, if the total nitrogen (3.406 per cent.) in beef round, laboratory No. 1850 (Table VI, p. 673) is multiplied by the factor 6.25 there is obtained the number 21.29, which represents the per cent. of proteid as obtained by the usual method of analysis. The total proteid obtained by actual analysis by the methods used in this investigation is only 18.60 per cent. (Table V, p. 672). This gives a difference of 2.69 per cent. Since the nutritive value of the organic extractives is certainly much less than that of proteids, the usual method of analysis and calculation must necessarily lead to erroneous results in reporting and considering the nutritive worth of meats and meat products.

The improved methods of analysis give the same information regarding the water and fat contents of meat as does the usual method. The former method enables the analyst to determine the soluble and insoluble mineral constituents of flesh.

Recently the methods of analysis here proposed have been extended so as to include the determination of the various forms in which the element phosphorus exists in meat. The data here presented are not sufficient to enter into a discussion regarding the amount and distribution of the different forms of phosphorus compounds in flesh. An extended study of the phosphorus contents of flesh is now well under way in this laboratory and the results of this research will be published in the near future.

In the fourth place, the methods of analysis here suggested show that marked differences exist in the chemical composition, between raw meats on the one hand and cooked meats on the other hand. By the use of this method of analysis it has been demonstrated that meats cooked by different methods possess quite a difference in chemical composition.

These facts are of practical importance, since they indicate plainly the nature of the chemical reactions and changes involved in the processes of the cooking of meats.

It is not the object of this paper to discuss this last-mentioned subject, but that the above statements are true, it can readily be seen by a brief study of the data presented in Table X, in which the chemical composition of raw and cooked meats is given, expressed in percentage of the water-free and fat-free substance. It is evident from the data here presented that the fat-free substance

of uncooked meats is much more soluble in cold water than is the fat-free material of cooked meats. It is also apparent that the soluble coagulable proteid, the total organic extractives, the ash and the phosphorus compounds exist in cooked meats in much smaller quantities than they do in uncooked meats. Further, the data here presented show clearly that there are marked differences in the chemical composition of meats cooked by roasting, pot-roasting and boiling.

The more complete information obtained by the application of these methods of analysis, regarding the chemical composition of meats, should aid in throwing considerable additional light upon the nutritive value and upon the ease and rapidity of the digestion and assimilation of different kinds of meat and of meats cooked by different methods.

If it is possible, as the writers fully believe it is, to apply this method of analysis with accuracy to the quantitative examination of meats and other food products, this fact should induce and encourage still further investigations to determine the comparative nutritive value between the soluble and the insoluble proteids, between the different forms of soluble proteids, and also, to study still further the functions which the nitrogenous and the non-nitrogenous organic extractives play in the processes of nutrition.

For the data given in the above tables only a few analyses were selected which represent the application of the methods herewith presented. In connection with the researches which are being made in this laboratory upon the chemistry of flesh, this method has already been used in the analysis of 150 samples of different kinds of raw and cooked meats, and other meat products. The detailed results of these analyses will be published in the near future.

I wish here to express my thanks to Messrs. F. W. Gill and J. M. Barnhart, for their valuable assistance in this research.

UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS.

[CONTRIBUTION FROM THE NEW YORK AGRICULTURAL EXPERIMENT STATION].

THE PROTEIDS OF CREAM, BUTTER AND BUTTERMILK IN RELATION TO MOTTLED BUTTER.

LUCIUS L. VAN SLYKE AND EDWIN B. HART.

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IN CONNECTION with our study of the action of acids upon milk-casein (calcium casein) it occurred to us that the results might have an application in some of the stages of butter-making. We have clearly established the fact that two distinct substances are formed in succession when calcium casein is brought into contact with an acid, whether it be the lactic acid produced in milk by the fermentation of milk-sugar, or some other acid, such as acetic, hydrochloric or sulphuric. When a small amount of acid is added to milk or to a preparation of calcium casein a precipitated substance unlike calcium casein is formed, this substance being soluble in a warm 5 per cent. solution of sodium chloride and also in hot 50 per cent. alcohol, and possessing characteristic properties of plasticity and ductility. This substance we were at first led to regard as a compound formed by direct combination of casein and acid, and we called it a casein mono-salt of the acid used as precipitant, but we have recently shown[1] that the compound is base-free casein. When this body is treated with an additional amount of acid a substance is formed which is insoluble in warm 5 per cent. salt solution, and nearly so in hot 50 per cent. alcohol and which has lost the plastic and ductile properties that characterize free casein. This substance we formerly regarded as a casein di-salt of the acid used to form it, in the belief that there were two series of precipitated salts formed by casein with an acid. Since our later work shows that there is only one series, this substance we now regard as simply a casein salt of the acid used as precipitant. The compound we formerly designated as casein monolactate is free casein or simply casein, and the body we previously called casein dilactate is casein lactate.

Since the presence of one or both of these compounds is necessarily involved in all operations where milk undergoes the change of ordinary souring, it seemed desirable to make a special study of the following points: (1) What, if any, relation these compounds

[1] Bull. 261, N. Y. Agr. Expt. Sta.

might have to the ripening of cream, preliminary to butter-making. (2) Which of these compounds was commonly present in butter and buttermilk? (3) Whether the occurrence of what is known as "mottling" in butter has any relation to either of these casein bodies.

The Relation of Casein and Casein Lactate to Cream-Ripening.—We wished first to ascertain what form of casein compound was obtained in the ripening of cream, when the cream showed different percentages of acid. Three series of experiments bearing on this point were made. Some fresh, pasteurized cream was treated with a carefully prepared starter in Erlenmeyer flasks, stoppered with cotton. These were allowed to stand at room temperature, samples being withdrawn for examination from time to time. The results of these experiments are given in the following table:

TABLE I.—SHOWING CHEMICAL CHANGES IN CREAM-RIPENING.

No. of experiment.	Age of cream when analyzed. Hours.	Amount of milk-sugar in cream. Per cent.	Amount of milk-sugar changed. Per cent.	Amount of lactic acid formed. Per cent.	Total amount of nitrogen in cream. Per cent.	Nitrogen in cream in form of casein and its compounds. Per cent.	Nitrogen in cream in form of casein lactate. Per cent.
1	Fresh	3.64	....	0.15	0.39	0.32	0.00
	8	3.58	0.06	0.18	0.39	0.31	....
"	24	2.92	0.72	0.60	0.38	0.33	0.33
"	32	2.90	0.74	0.61	0.39	0.30	0.30
"	48	2.88	0.76	0.62	0.39	0.32	0.32
"	72	2.90	0.74	0.63	0.38	0.34	0.34
2	Fresh	3.84	....	0.14	0.41	0.34	0.00
2	24	3.04	0.80	0.64	0.40	0.35	0.35
3	Fresh	3.81	....	0.14	0.41	0.35	0.06
"	24	2.93	0.88	0.70	0.40	0.36	0.36

The following statements are suggested by the data contained in Table I:

(1) *Nitrogen Compounds in Ripened Cream.*—When the cream was fresh and when it was eight hours old there was only calcium casein (milk-casein) present; that is, neither of the compounds (free casein and casein lactate) formed from calcium casein by treatment with lactic acid was present. In twenty-four hours the only casein compound present in the cream was casein lactate, the compound insoluble in warm dilute salt solution; this is the compound commonly observed in milk curdled by ordinary sour-

ing. In each of these experiments the cream had curdled completely to a definite coagulum. It would, therefore, appear that in ordinary methods of cream-ripening, when the lactic acid is allowed to reach 0.6 per cent., neither calcium casein nor free casein is present, but only casein lactate, the substance most commonly observed as curdled sour milk.

(2) *Decrease of Milk-sugar in Cream-ripening.*—In the three experiments the milk-sugar decreased to an extent varying from 0.72 to 0.88 per cent. in twenty-four hours. In the first experiment, which was continued seventy-two hours, the amount of milk-sugar decreased very little after twenty-four hours.

(3) *Formation of Lactic Acid in Cream-ripening.*—When the cream was fresh the apparent amount of lactic acid was only 0.14 or 0.15 per cent., which increased in twenty-four hours to 0.6 to 0.7 per cent. In the first experiment, which was continued seventy-two hours, the acid increased very little after twenty-four hours.

In connection with these experiments it may be mentioned that, in several lots of cream ripened so as to show an acidity of 0.38 to 0.43 per cent., we found much free casein and little casein lactate.

The Acidity of Milk and Cream.—It may be well in this connection to call attention to the inaccuracy involved in attributing the acidity of milk or cream to lactic acid alone. The usual method of determining acidity in milk or cream is to titrate a given amount of milk with a standardized solution of fixed alkali, using phenolphthalein as an indicator, the alkali being added to the milk until a fairly permanent pink color appears. Lactic acid is not the only compound in milk that neutralizes alkali. It is well known that strictly fresh milk, which contains no lactic acid, neutralizes an appreciable amount of alkali. The compounds in fresh milk or cream that have the power of neutralizing alkali are the following: (1) Calcium casein (milk-casein), (2) acid phosphates and citrates, and (3) carbon dioxide. Of these the calcium casein and acid phosphates appear to be most prominent. While results vary with individual cows, the average amount of acidity of fresh milk is about 0.08 per cent., calculated as equivalent to lactic acid. If one desires to estimate more closely the amount of real lactic acid in milk, it is necessary only to subtract from the results commonly found, 0.1 per cent. Just how much deduction should be made in case of cream it is more difficult to say. For

ordinary work in creameries such distinctions are not essential.

Therefore, in the results given in Table I we have not stated the absolute amount of lactic acid present in the cream, but the results in the form given are more readily comparable with the results obtained in creamery work.

The Relation of Calcium Casein, Casein and Casein Lactate to the Proteids of Butter and Buttermilk.—The curd present in butter is casein lactate when the amount of lactic acid formed in cream-ripening exceeds 0.5 per cent. In butter made from cream ripened so as to contain less than 0.5 per cent. of acid the same compound of casein is apt to be present ultimately in the butter, especially if buttermilk is left in the butter to any extent, because the milk-sugar present in the buttermilk remaining in the butter is changed in time to lactic acid, which acts upon any calcium casein or free casein in the butter, producing finally the compound usually present in butter made from well-ripened cream.

In butter made from sweet cream we find in the butter essentially calcium casein with, perhaps, some free casein. With sufficient milk-sugar incorporated in such butter through the presence of buttermilk we may have at different times any one, or a mixture, of the following compounds of casein: (1) Calcium casein, (2) calcium casein and free casein, (3) free casein and casein lactate, and (4) casein lactate. It is hardly probable that we should often find calcium casein alone in sweet-cream butter, as it is commonly made, though it would be possible to make the butter so that it would contain only calcium casein. In ordinary sweet-cream butter, when fresh, we commonly find a mixture of the two forms, calcium casein and free casein. Later, after the formation of more lactic acid, we may have free casein alone, which, with increasing amounts of lactic acid, will gradually be changed into casein lactate, the form commonly present in commercial butter made from ripened cream.

The amount of milk-albumin in normal butter is very minute under any conditions.

The curd of different butters and of the same butters at different ages presents quite different appearances. For special examination of its properties the curd of butter is obtained by dissolving the butter at as low a temperature as practicable and allowing the curd and brine to settle beneath the layer of butter-fat. The curd prepared from fresh butter, made from cream having an

acidity of 0.5 or 0.6 per cent., is gelatinous in appearance and does not readily separate into small particles on standing. The curd of butter that is a few weeks old often appears granular. This is due, as we shall point out later, to the action of salt upon the physical properties of the casein lactate.

The Relations of the Proteids of Butter to the Mottling of Butter.—One of the common defects of butter is more or less marked variation in color, or what is technically called "mottles," showing in the form of white streaks, waves, spots or blotches. It has been universally believed that these light-colored portions are caused by uneven distribution of salt, the more concentrated brine deepening the yellow color of the fat, and the lighter portions being the unsalted or lightly salted areas.

We have studied the following conditions of manufacture in their relation to mottled butter: (1) Richness of cream, (2) degree of ripeness of cream, (3) temperature of churning, (4) size of butter granules, (5) temperature of wash-water, and (6) working of butter. The results of this work indicate that when the churning is managed so as to make the butter-granules of the size of rice-grains and these are carefully washed twice with water below 7° C., removing most of the buttermilk adhering to the outer surface of the granules, no mottles appear, however conditions are varied in other respects. Mottles are always found when the buttermilk is not sufficiently removed.

The Cause of Mottles in Butter.—The fact that we have no mottles in butter when we have no salt has led to the belief that the salt is the sole cause of mottles and produces mottles as the result of its uneven distribution. It is held that the salt deepens the color of the butter-fat, the lighter portions containing little or no salt, the darker portions containing salt.

Effect of Salt on Color of Butter-fat.—We desired to test the question experimentally whether salt brine has any influence on the color of butter-fat. We took some fresh, colored, unsalted butter, melted and filtered it in order to separate the butter-fat from the other constituents of the butter. The filtered portion was allowed to harden and then cut into cubes and immersed in 30 per cent. brine in such a way that a part of the cube was in brine and a part out. There was not the slightest increase of depth of color or any other change in color noticeable.

In another experiment some butter-fat was stirred with salt. The mixing produced a variegated color, not a true mottling, due to the grains of undissolved salt. The same effect is produced by mixing any white substance, sugar for instance, with butter-fat.

It would, therefore, appear that the mottling of butter is not produced by salt in the way generally held, *viz.*, by affecting the color of the butter-fat itself.

Amount of Salt in Mottled and Unmottled Butter.—We took samples of butter by means of a trier, taking a plug through the ends of the prints examined. In one sample of unmottled butter the amount of salt at opposite ends of a pound print was 3.65 and 2.61 per cent. In another unmottled butter the salt varied from 4.6 to 5.3 per cent., and in still another from 1.86 to 2.59. In some badly mottled butter the salt at different ends of some prints varied from 5.13 to 5.19 and 4.66 to 4.73, which showed very even distribution of salt. We may, then, have mottles where the salt is evenly distributed, and no mottles where the salt is unevenly distributed. Samples taken in the manner indicated by a trier give only the average of the mass, but do not enable one to distinguish the amounts of salt in the lighter and darker portions separately.

Amount of Salt in Light and Dark Portions of Butter.—It is a matter of common experience that the lighter portions of mottled butter appear to the taste to contain less salt than the darker portions. We examined two samples of mottled butter, determining the amount of salt in the different colored portions when the butter was twenty-four hours old. The butter was somewhat overchurned purposely to produce conditions for mottling. The washing, salting and working were done in the usual way. The two butters gave the following results:

Butter	1, light portion	.....	0.91	per cent.	of	salt.
"	1, dark "	.....	5.45	"	"	"
"	2, light "	.....	0.70	"	"	"
"	2, dark "	.....	6.74	"	"	"

These results agree with the sense of taste in showing that the lighter portions contain less salt than the darker portions of the butter.

Distribution of Brine in Butter on Standing.—In order to learn to what extent the salt of butter becomes more evenly distributed

on standing, we determined, at intervals, the salt in the different colored parts of same butters referred to in the preceding paragraph. The results are as follows:

	24 hours.	48 hours.	5 days. Salt. Per cent.
Butter 1, light portion.....	0.91	1.79	1.40
" 1, dark "	5.45	5.94	6.22
" 2, light "	0.70	1.69	1.69
" 2, dark "	6.74	6.04	6.22

These results indicate that after twenty-four hours the tendency of the salt to distribute itself more uniformly through the mass of butter is not very marked. The differences indicated may come mostly from variation in the samples examined.

The Amount of Proteid in Mottled and Unmottled Portions of Butter.—The amount of proteid was determined in mottled and unmottled portions of several butters and the results are as follows:

No. of experiment.	Proteid in light portion of butters. Per cent.	Proteid in dark portion of butters. Per cent.
1.....	1.30	0.76
2.....	0.76	0.14
3.....	0.76	0.36
4.....	0.63	0.25
5.....	0.86	0.31
Average.....	0.86	0.36

These results indicate that the light portions of butter contain more casein lactate than the deeper colored portions. This casein lactate comes from retention of buttermilk. It is generally noticed that in working butter the liquid coming from the worker is turbid and milky when the buttermilk has not been removed, while it is more or less clear when the buttermilk has been properly washed out of the granules before salting and working.

The Amount of Water in Mottled and Unmottled Butters.—The determination of water in mottled and unmottled butters gave the following results:

Water in mottled butter. Per cent.	Water in unmottled butter. Per cent.
13.03	12.87
13.00	10.52
11.97	10.50
15.35	12.00
15.50	13.30
Average, 13.77	11.84

The mottled butters vary greatly among themselves as well as the unmottled in respect to content of water. The larger amount of water in these mottled butters is the result of the retention of more buttermilk.

Properties of Proteid in Butter and Buttermilk.—The chief proteid of butter made from ripened cream is casein lactate. In fresh sweet-cream butter the chief proteid is calcium casein (milk-casein) with more or less free casein. On standing, these constituents may change, forming more largely a mixture of free casein and casein lactate and, if milk-sugar is present to form sufficient acid, casein lactate entirely. The proteids of fresh buttermilk are the same as those contained in the butter, and the exact kind and amount depend upon the amount of acid formed. In ordinary buttermilk, in which the proteid is casein lactate, we notice that the proteid exists in fine particles in suspension. When buttermilk is treated with salt so as to form a brine about equal to that of normal butter, the salt causes the proteid to condense or concentrate in a more or less solid mass. This effect of salt is readily shown in the accompanying illustration. In the samples containing 20 per cent. or more of salt the proteid has separated in a marked manner. This same action takes place whether the proteid is calcium casein, casein or casein lactate. This action appears to be a purely physical one; the brine seems to harden the particles of proteid and cause the proteid mass to contract into less space in the tubes.

Relation of Time to Formation of Mottles.—It is well known that the light-colored portions do not appear in butter at once after adding salt and working the butter, but several hours are required to develop them and the maximum development occurs after about twenty-four hours in our experience. In the experiments in which we treated buttermilk with salt the separation or condensation of the proteid by the brine was not complete until twenty-four hours had elapsed.

Relation of Proteids of Butter to Mottles.—The facts presented in the foregoing pages appear to us to furnish a satisfactory explanation of the causes of mottles in butter. Reviewing these facts we have seen that:

(1) Salt brine does not change in any way the color of butter-fat.

0
5
10
20
30
35

(2) The amount of salt may vary considerably in different portions of butter that is not mottled.

(3) In different portions of badly mottled butter the distribution of salt may be very uniform throughout the mass of butter as a whole.

(4) In mottled butter the light portions usually contain less salt than the darker portions.

(5) Mottles proper do not occur in unsalted butter.

(6) The amount of proteid in mottled butter is greater in the light portions than in the portions of normal color.

(7) Unsalted butter, containing buttermilk adhering to the outer surface of the granules, mottles on the surface when submerged in concentrated salt brine.

(8) Mottling does not occur in butter when the buttermilk, adhering to the outer surface of the small granules, is mostly removed.

(9) Small butter granules (rice-size) washed with water at low temperature lose most of the adhering buttermilk and no mottles appear in the finished butter in the presence of salt.

(10) Large granules or chunks favor the retention and uneven distribution of buttermilk and we get mottles in the finished butter.

(11) Salt brine, as it usually occurs in butter, has the power of hardening and localizing the proteid (usually casein lactate) of butter. The action requires several hours.

From these facts it would appear that mottles in butter are due, primarily, to the presence and uneven distribution of buttermilk adhering to the outer surface of the small granules, and, secondarily, to the effect of salt brine upon the proteid of the buttermilk thus retained in butter. In the absence of either salt or excess of buttermilk we have no mottling. Moltting occurs most frequently as the result of an uneven distribution of buttermilk in the presence of salt distributed either evenly or unevenly. Mottling may be produced by an uneven distribution of salt in the presence of an excess of buttermilk even when uniformly distributed. In general, those conditions that favor the elimination of excess of buttermilk or its even distribution do not favor mottles, while those conditions that favor the retention and uneven distribution of buttermilk in butter favor the formation of mottles in the presence of salt.

Theoretical Considerations Relating to the Formation of Mottles in Butter.—We have presented the facts showing that the formation of mottles in butter is due primarily to the presence and uneven distribution of an excess of buttermilk adhering to the outer surface of the small butter granules, and, secondarily, to the action of salt brine upon the proteid of the buttermilk thus retained in butter. We desire to consider a little more fully how the action takes place.

A mass of butter must be regarded as an aggregation of butter-granules more or less loosely compacted. There is a variable amount of space between the granules and in these interstices we find the salt brine and also the buttermilk that is left adhering to the outer surface of the granules. There exist, therefore, more or less extensive channels through which movement of brine or buttermilk may take place to a limited extent when conditions favor any movement. The brine present in freshly packed butter does not necessarily remain, each particle, in the exact position in which it is left when packed and not subject to any further mechanical manipulation. The conditions that favor movement or limited circulation of the brine in butter are an unequal distribution of salt brine and buttermilk, producing a variation in the specific gravity which tends thus to become uniform within limited areas. When there is an imperfect removal of the buttermilk adhering to the outer surface of the small butter-granules the buttermilk is unevenly distributed, being more or less localized in different portions of the mass of butter. When the salt brine comes into contact with these masses of buttermilk the casein lactate is slowly acted upon by the brine, being hardened and remaining localized. The yellow or clear portions occur where the spaces between the butter-granules are filled with clear brine and are comparatively free from casein compounds. The fact that time is required to produce mottles is explained, first, by the time required for the movement or circulation of brine to take place and come in contact everywhere with the casein compounds, assuming that this has not occurred in the working of the butter, and, second, by the amount of time required for brine to act upon the casein compounds of butter.

The discussion presented in the foregoing paragraph is, apart from the facts that have been clearly established, intended as a theoretical explanation or suggestion of what takes place when

mottles form in butter. While the data presented point to the fact that there is some movement of brine in packed butter, the matter has not been studied in sufficient detail to justify any specific statements. Such a study is attended with serious difficulties, but we plan to make further investigation of this phase of the subject.

SUMMARY.

(1) *Points Investigated.*—The questions studied in this paper are: (*a*) The relation of casein compounds to cream-ripening; (*b*) casein compounds present in butter and buttermilk; (*c*) the relation of casein compounds to mottled butter.

(2) *Casein Compounds in Ripened Cream.*—In ordinary methods of cream-ripening neither calcium casein nor free casein is present, but only casein lactate, when the lactic acid is allowed to exceed 0.5 per cent. Casein lactate is the substance most familiar as curdled sour milk.

(3) *Casein Compounds in Butter and Buttermilk.*—When the amount of lactic acid in cream exceeds 0.5 per cent. the casein in the butter and buttermilk is present as casein lactate. In butter and buttermilk made from so-called sweet cream we usually find calcium casein and some free casein, and on standing for some weeks these may be changed in the butter into a mixture of free casein and casein lactate or wholly into casein lactate.

(4) *Views Commonly Held in Respect to Cause of Mottled Butter.*—It has been quite universally believed that the light spots or streaks in butter, known as mottles, are caused by the uneven distribution of salt, the more concentrated brine deepening the yellow color of the fat and the lighter portions being the unsalted or lightly-salted areas.

(5) *Points Studied in Relation to Mottled Butter.*—The investigation covered the following conditions in relation to the mottling of butter: (*a*) *Richness of cream,* (*b*) degree of ripeness of cream, (*c*) temperature of churning, (*d*) size of butter-granules, (*e*) temperature of wash-water, (*f*) working of butter.

(6) *Results of Investigation of Preceding Conditions.*—When the churning was managed so as to make the butter-granules of the size of rice-grains and these were carefully washed twice with water below 45° F., removing most of the buttermilk adhering to the outer surface of the granules, no mottles were obtained; however,

conditions were varied in other respects. Mottles were always found when the buttermilk was not sufficiently removed.

(7) *Relation of Proteids to Mottled Butter.*—The amount of proteid (casein lactate) in mottled butter is greater in the light portions than in the darker portions, and is the cause of the lighter color of the mottles.

(8) *Relation of Salt to Mottles.*—(*a*) Salt brine does not change in any way the color of butter-fat. (*b*) Salt brine, as it commonly occurs in butter, has the power of hardening and localizing the proteid particles, the action requiring several hours for completion. (*c*) Butter, free from buttermilk adhering to the outer surface of the granules, does not produce mottles when salted, whether the salt is evenly or unevenly distributed. (*d*) Mottles do not occur in unsalted butter. (*e*) In mottled butter the light portions usually contain less salt than the darker portions.

(9) *Cause of Mottled Butter.*—Mottles in butter are due, primarily, to the presence and uneven distribution of buttermilk adhering to the outer surface of the small granules; and, secondarily, to the hardening and localizing effect of salt brine upon the proteid of the buttermilk thus retained in butter. The light portions of mottled butter owe their lighter color to the presence of localized proteid (usually casein lactate). The yellow or clear portions occur where the spaces between the butter-granules are filled with clear brine and are comparatively free from casein compounds. Several hours are required to complete the action of the brine upon the proteid of the butter.

(10) *Prevention of Mottles in Butter.*—Mottles in butter can be prevented by avoiding those conditions that retain buttermilk in the butter and observing those conditions that favor the removal of buttermilk from butter-granules before salting. The butter-granules should be about the size of rice-grains and should be washed twice with water at a temperature of 35° to 45° F.

[Contribution to the Chemistry of Sugar Analysis, No. 2].

THE COMMERCIAL ANALYSIS OF CANE MOLASSES. I. OPTICAL METHODS.

By Harris E. Sawyer.

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It seems to be assumed by many commercial analysts that the routine methods which they employ in the examination of molasses will yield comparable and trustworthy, even though not wholly accurate, results. There is serious doubt, however, whether such an assumption is warrantable. In the writer's opinion it is not. Reports in his possession, from several laboratories to which similar collections of molasses samples had been sent for examination, are so divergent in their results as to make it impossible to decide, not only as to the actual, but even as to the relative, saccharine strengths of the different samples.[1] It may be reason-

Analysts.	S.	P.	G.	K.
Sample 1.	28.60	30.0	32.0	30.0
	25.00	*22.7*	*24.5*	*20.2*
	53.60	52.70	56.5	50.2
Sample 2.	22.0	22.6	23.4	26.0
	26.88	*26.0*	*27.7*	*24.87*
	48.88	48.6	51.1	50.87
Sample 3.	26.40	27.1	29.4	28.80
	25.64	*24.4*	*25.7*	*24.25*
	52.04	51.5	55.1	53.05
Sample 4.	21.60	22.6	25.8	20.0
	28.09	*27.8*	*28.4*	*26.21*
	49.69	50.4	54.2	46.21
Sample 5.	25.0	26.0	28.2	24.4
	29.76	*29.0*	*29.4*	*26.94*
	54.76	55.0	57.6	51.34

[1] The three quantities reported for each analysis in the following tabulation represent respectively the percentages of cane-sugar, reducing sugars, and the total sugars of the samples. The reducing sugar percentages are printed in italics.

able to ascribe these divergences in part to careless manipulation; but since the analyses were made by firms specializing in saccharimetry, it seems fair to presume that carelessness could not have been the only source of error, and that variation in, and inadequacy of, the analytical methods employed must also be held responsible for part of the disagreements.

In fact, many sources of inaccuracy have been discovered in the customary methods of sugar analysis; and various means have been proposed, especially in foreign publications, for their removal. But since these methods of greater accuracy have never been combined in the form of a convenient routine procedure, available for daily use in commercial testing laboratories, and since, furthermore, cane-molasses of the poorer grades was for years a practically worthless waste material, little real progress has been made in this country toward the general adoption of more accurate methods for its valuation.

Of late, however, on account of the increasing utilization of molasses as a fodder and as a raw material for the production of alcohol, the value of even the poorest grades has undergone a sharp advance; and for this reason increased precision in analysis is daily becoming more essential. Led by this consideration, the writer began, four years ago, a careful examination of the existing analytical methods, hoping to find a procedure simple and quick enough for routine work, and capable, at the same time, of determining the total sugar of a sample with an error not exceeding about ± 0.5 per cent. A method which seemed to satisfy these conditions fairly well was soon found, and was outlined in 1903 in a preliminary note addressed to the Association of Official Agricultural Chemists.[1] It is presented herewith in detail, together with the results of further study to which the writer has subjected it since that time.

THE COMPOSITION OF TYPICAL CANE-MOLASSES.

It is necessary, before discussing the procedure in question, and the writer's work thereon, to consider the character of the material in whose examination it is to be applied, and the influence of variations in that character as a source of error in existing analytical methods.

Obviously, it is impossible to make any sharp classification of the many varieties of cane-molasses, since, from the nearly color-

[1] Bulletin 81, Bureau of Chemistry, U. S. Dept. of Agr., p. 175.

less table syrups on the one hand to the tarry "black-strap" residuums on the other, they merge into each other by almost imperceptible differences of character. It is legitimate, however, to refer cane-molasses of any kind to some one of three types, *e. g.*, the "first," "second" and "third" molasses of the sugar plantation.[1] It therefore is sufficient for the purposes of this discussion to describe these types, and to consider their characteristic behaviors with relation to analytical processes as illustrative of the behavior of molasses in general.

The relative character of these three types of molasses is well shown by the following tabulations, based on data from a report by Edson.[2]

TABLE I.

		Total solids.	Direct polarization.	Sucrose.	Reducing sugars.	Non-sugars.
Second plant run. P. 35.	First molasses ...	71.56	55.7	58.06	10.39	3.11
	Second " ...	76.7	33.4	36.99	21.34	18.37
	Third " ...	78.8	23.2	29.11	29.36	20.33
Third plant run. P. 39.	First molasses ...	71.88	53.8	54.97	11.57	5.34
	Second " ...	77.5	36.8	39.96	20.10	17.44
	Third " ...	77.6	22.0	26.62	28.52	22.46

It must be borne in mind that the foregoing figures represent types only, and not standards of composition. Naturally, the composition of cane juice varies considerably from season to season and from place to place. Furthermore, manufacturing processes are not everywhere the same; mechanical appliances are liable to differ in design and efficiency, and the skill and care displayed in their management may vary widely. For these reasons there inevitably must be considerable variations in the composition of molasses of any type. But admitting this, it still is clear that

[1] For readers who are not acquainted with the terminology of sugar manufacture, the following explanation may be useful. Cane juice, after being "defecated" or freed of certain impurities, is evaporated to a thick syrup and is allowed to crystallize. The magma so obtained, called the "first massecuite," is separated by centrifuging into its constituents, the "first sugar" and "first molasses." The molasses, which still contains a large amount of recoverable sugar, is evaporated again, usually after a clarification of some kind, and a "second massecuite" is thus obtained, which in its turn is separated into the "second sugar" and "second molasses." In many localities, the extraction of sugar is abandoned at this point. In Louisiana, however, it is customary to reboil the second molasses and thus to obtain a "third sugar" and a "third molasses." There is also, in this country, at least one refinery which imports West Indian "seconds" for reboiling in this manner.

[2] Record of experiments at the Sugar Experiment Station on Calumet Plantation, Pattersonville, La. Bull. 23, Bureau of Chemistry, U. S. Dept. of Agr., 1889, pp. 35 and 39.

each type has characters which differentiate it unmistakably from its fellows.

Thus, first molasses is characterized by a high direct polarization and a high percentage of sucrose, both usually well above 40°, and close together, and by a small percentage of non-sugars, usually less than 10 per cent. The proportion of reducing sugars, which may vary between 10 and 20 per cent., is not specially characteristic.

Second molasses is characterized by a lower polarization and sucrose percentage, and by a higher proportion of non-sugars. Its direct polarization usually lies between 30° and 36°, while the percentage of sucrose is some degrees higher, commonly between 36 and 44 per cent. The non-sugars may range between 15 and 21 per cent., but are most likely to be in the neighborhood of 18 per cent. Second molasses contains a somewhat larger proportion of reducing sugars than first molasses, commonly between 15 and 22 per cent.; but as in the case of first molasses, their amount is not specially characteristic.

Third molasses usually shows a very low polarization, rarely above 25° and often as low as 15°. It commonly contains, however, from 25 to 30 per cent. of sucrose—more by 7 to 10 per cent. than would be shown by the direct polarization alone. Its proportion of non-sugars is materially higher than that of second molasses. These bodies amount usually to 23 to 25 per cent., and may increase at times to 33 to 35 per cent. As in the case of first and second molasses, the proportion of the reducing sugars has less significance. Ordinarily, however, they are more abundant than in second molasses, and they amount normally to 25 to 30 per cent.

The subjoined data, taken from the writer's laboratory records, show the resemblance of molasses in the Boston market to the foregoing types.

From the standpoint of the sugar-maker the essential difference between the three types of molasses just described is the progressive falling-off in the proportion of sucrose and in the coefficient of purity as we pass from "first" to "third." More significant, however, from the analyst's standpoint, and therefore for the purposes of this discussion, is the simultaneous increase in the proportions of reducing sugars and non-sugars, accompanied by lengthening of the interval between direct polarization and sucrose

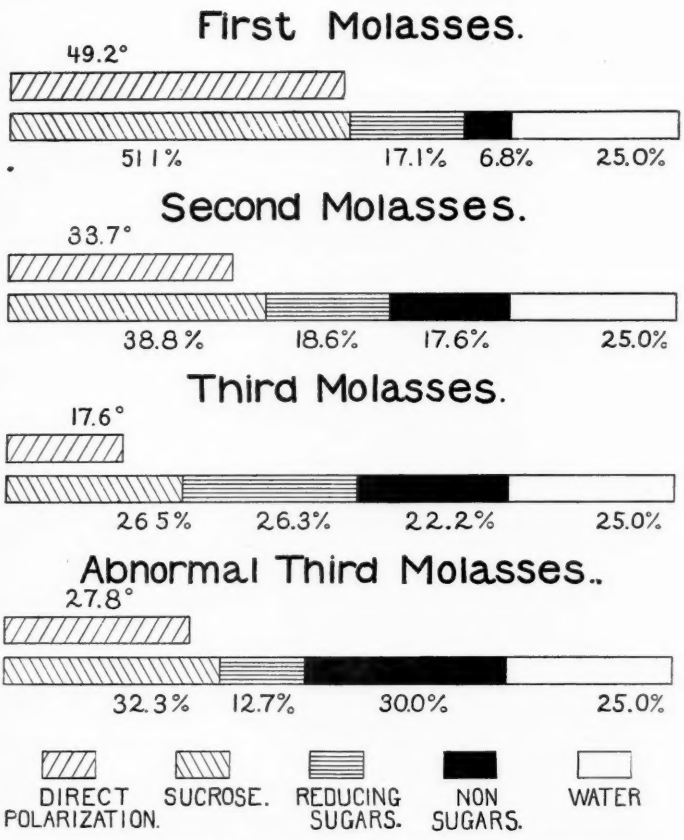
TABLE II.

	Total solids.[1]	Direct polarization.	Sucrose.	Reducing sugars.	Non sugars.[2]
		Firsts.			
1.	72.5	42.24	46.45	20.6	5.45
2.	74.7	44.7	45.9	20.8	8.0
3.	72.0	46.3	46.87	16.70	8.43
4.	72.9	43.0	44.1	19.2	9.6
		Seconds.			
5.	77.0	36.7	43.0	20.6	13.4
6.	76.9	35.0	40.3	21.5	15.1
7.	80.0	37.0	41.7	22.4	15.9
8.	77.8	32.7	39.1	22.3	16.4
9.	79.3	33.0	40.4	21.6	17.3
10.	75.0	32.0	38.2	17.8	19.0
11.	82.9	36.3	43.6	19.8	19.5
12.	78.8	34.7	39.1	19.0	20.7
13.	75.7	31.8	35.8	18.3	21.6
14.	82.2	38.3	43.2	17.2	21.8
15.	81.9	41.9	43.7	15.4	22.8
		Thirds.			
16.	76.5	17.0	26.6	29.1	20.8
17.	81.3	17.0	26.9	33.3	21.1
18.	79.2	23.5	32.1	25.8	21.3
19.	80.3	20.1	29.2	27.7	23.4
20.	79.7	19.5	28.0	28.2	23.5
21.	80.2	17.6	28.0	28.7	23.5
22.	80.2	18.2	27.3	27.1	24.0
23.	83.4	20.3	30.8	28.0	24.6
24.	79.9	16.1	28.2	26.8	24.9
25.	80.2	18.2	27.3	27.1	25.0
26.	79.5	20.0	27.2	27.2	25.1
		Abnormal Thirds.[3]			
27.	80.2	28.7	34.3	16.0	29.9
28.	81.0	29.0	34.8	15.7	30.5
29.	80.6	31.1	35.2	11.6	33.8
30.	82.4	32.2	35.5	11.4	35.5

[1] The values in this column do not represent the true percentages of total solids, as determined by the difficult process of desiccation and weighing, but the "Brix degree" of the samples,—an approximation to, and somewhat higher than, the true value.

[2] Non-sugars = Brix (Total solids)—(Sucrose and reducing sugars).

[3] Whereas the "thirds" of the foregoing tabulation represent the run of the market, the "abnormal thirds" represent different lots of the final residuum of a single molasses refinery, whose product is always characterized by a percentage of sucrose abnormally high for third molasses, by an exceptionally low percentage of reducing sugars, and by an excessive proportion of gums, ash, and decomposition products.



This diagram represents the average of the molasses analyses shown in the tabulation on p. 696, Edson's two samples of "first molasses" being included with the writer's four samples. To facilitate comparison, all of the averages have been recalculated to a uniform content of 25 per cent. of water.

percentage, and by marked intensification of color. The bearing of the latter facts upon the choice of analytical procedure is most important, and has received heretofore too little consideration on the part of commercial chemists.

THE CUSTOMARY METHODS OF COMMERCIAL MOLASSES ANALYSIS.

It is the usual practice in testing raw sugars to assume that the

direct polarization represents the percentage of sucrose, and to avoid in this way the added manipulation involved in Clerget's double polarization method. The character of the errors likely to be introduced by acting on this assumption is shown by the accompanying tabulation of results obtained in the writer's laboratory.

TABLE III.

Sample.	Sucrose by Single polarization.	Sucrose by Double polarization.	Difference.[1]
Cuban centrifugal.....	96.85	97.00	+0.15
Java "	96.40	95.83	—0.57
San Domingo centrifugal	97.16	97.35	+0.19
Cuban second sugar.....	91.23	90.80	—0.43
Muscovado 1.....	90.50	90.90	+0.40
" 2.....	88.20	89.00	+0.80
" 3.....	92.10	91.40	—0.50
" 4.....	86.54	86.00	—0.54
	Mean of —differences		—0.51
	" " + "		+0.39
	" " all "		—0.06

It will be seen from the foregoing figures that, although the direct and double polarization values for sucrose may differ for any individual sugar sample by about ±0.5 per cent., the mean of these differences becomes very small when a number of samples are examined. In the end, therefore, use of the double polarization method would probably add but little to the accuracy of sugar-testing.[2]

Since the "single polarization" procedure works well in the examination of raw sugars, many chemists have assumed that it also may be adopted legitimately in the analysis of cane-molasses;[3]

[1] While these differences unquestionably are due in part to experimental error, it is most improbable that such error is responsible for more than a small part of any of them, since they are not altered materially by making careful duplicate analyses. Similar differences are shown by results obtained in the laboratory of the Bureau of Chemistry (Bull. **13**, "Foods and Food Adulterants," Part 6: "Sugar, Molasses and Syrup, Etc.," p. 672) and by Nasini and Villavecchia (Sul peso normale pei saccarimetri. Publio. de lab. chim. centr. delle gabelle, Rome, 1891, pp. 28-29).

[2] Indeed, it is likely that the true percentage of sucrose may be more nearly represented by the direct polarization than by the quotient obtained after double polarization, since the latter value is far more liable to be affected by experimental error.

[3] Aime Girard and Laborde: *Comptes rendus*, 1876, p. 214; 1877, p. 800; Morin: *Ibid.*, 1877, p. 802; Beaufret: *Bull. de l'Ass'n des Chimistes*, **13**, 133; see also, for criticism of the foregoing writers, Pellet: *Bull. de l'Ass'n des Chimistes*, **13**, 757; Pellet and Barbet: *Ibid.*, **13**, 948.

and, indeed, for certain purposes it often may be followed without the introduction of serious error. The following tabulation, which summarizes the six analyses of first molasses already reported, shows that the mean error due to the difference between the direct and double polarization values is usually very small for goods of this grade.

TABLE IV.

First molasses.	Sucrose by Direct polarization.	Sucrose by Double polarization.	Errors.
Edson	55.70	58.06	2.36
"	53.80	54.97	1.17
No. 1.....	42.24	46.45	4.21
" 2.....	44.7	45.9	1.2
" 3.....	46.3	46.87	0.57
" 4.....	43.0	44.1	1.1
Means.....	47.62	49.39	1.77

Such first molasses as comes upon the market is ordinarily destined for the grocery trade, and since its value for this purpose is fixed by color and flavor rather than by the percentage of sugar which it may contain, understatement of the sucrose by 2 or 3 per cent. may be of little importance in a trade analysis.[1] Moreover, the minus errors shown by the tabulation are reduced somewhat by other errors of opposite sign, due to the method employed in preparing the solution for analysis, and having the effect of raising the direct polarization.

As is well known, molasses is prepared for polarization by dissolving a definite amount—usually the so-called "normal weight"—in a little water, adding lead subacetate solution until satisfactory decolorization is produced, making the volume of the mixture up to some definite quantity—usually 100 cc.—and filtering. Obviously, the volume of the solution is less than the definite final volume of the mixture, inasmuch as a certain part of this space is occupied by the precipitate of lead and coloring-matters; and on this account the concentration and polarization of the solution are increased somewhat beyond their proper values.[2] Methods have been proposed by Scheibler[3] and by Sachs[4] for correction of

[1] Of course it is necessary for the food analyst, searching for added glucose, always to use the Clerget method for sucrose.

[2] Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, p. 102: Spencer's "Handbook for Sugar Manufacturers," p. 47.

[3] *Ztschr. Ver. Rubenzucker Industrie*, **25**, 1054 (1875).

[4] *Ibid.*, **30**, 229 (1880).

the error due to the bulk of this precipitate, which may be very considerable in the case of materials containing large proportions of coloring-matter.[1] The writer has employed the Scheibler "double dilution" method in the examination of several samples of molasses, with the following results:

TABLE V.

	Bulk of lead precipitate. cc.	Plus error.	Direct polarization. Observed.	Direct polarization. Corrected.
First Molasses:[2]				
No. 1.....	0.33	0.14°	42.24°	42.10°
No. 3.....	0.53	0.24°	46.30°	46.06°
Second Molasses:				
Cuban No. 2...	2.64	0.84°	31.92°	31.08°
Cuban No. 4...	2.64	0.96°	36.20°	35.24°
Third Molasses:				
No. 119.....	4.58	0.79°	17.68°	16.87°
A—C.....	5.20	0.94°	18.06°	17.12°
McCahan.....	4.00	1.13°	28.16°	27.03°

It is evident that sucrose percentages calculated on the basis of uncorrected polarizations will bear the same ratios to the true sugar percentages as the observed polarizations bear to the corrected ones. The following tabulation shows, in addition to the foregoing polarizations, the uncorrected and corrected percentages of sucrose in the same samples of molasses, together with the error which would be caused in each case by assuming that the uncorrected polarization represented the actual sucrose content of the sample.

TABLE VI.

	Direct polarization. Observed.	Direct polarization. Corrected.	Sucrose percentage. Uncorrected.	Sucrose percentage. Corrected.	Error.
First Molasses:					
No. 1.....	42.24°	42.10°	46.45°	46.31	—4.07
No. 3.....	46.30°	46.06°	46.87	46.63	—0.33
Second Molasses:					
Cuban No. 2.	31.92°	31.08°	36.16	35.21	—3.29
Cuban No. 4.	36.20°	35.24°	41.40	40.50	—4.30
Third Molasses:					
No. 119.....	17.68°	16.87°	29.50	28.21	—10.53
A–C.....	18.06°	17.12°	27.40	25.97	—7.91
McCahan....	28.16°	27.03°	32.22	30.93	—2.77

[1] Wiechmann, *Bull. de l'Ass'n des Chimistes*, **21**, 631 (1903), and Horne, This Journal, **26**, 186 (1904), have shown that the plus error introduced in the polarization of a raw sugar, through failure to correct for the bulk of the lead precipitate, may amount to 0.05°–0.98° Ventzke.

[2] Sachs' method, applied to these two samples of first molasses, gave practically identical results, the bulks of the lead precipitates being respectively 0.40 cc. and 0.60 cc., instead of 0.33 cc. and 0.53 cc.

Comparison with the values given in Table IV (p. 698) shows that the errors given therein for samples 1 and 3 have been slightly reduced through operation of the "precipitate error."

As has been said, it may be legitimate in some cases to determine the cane-sugar of first molasses by single polarization; but, on the contrary, it is bad practice to follow the same procedure in testing second and third molasses. Goods of the latter grades are valued according to their saccharine strength, and errors which may amount to a tenth or more of the total sucrose, as in the case of second molasses, or to a third of the total sucrose, as in the case of Sample 119, are not to be tolerated. It will not do to say that a constant correction may be applied to the direct polarization of low-grade molasses in order to approximate the true percentage of sugar; for as is shown by the three "third" samples of the foregoing tables, the errors are far from being constant. The only safe procedure, therefore, is to determine the sucrose by double polarization, and to take account of the error due to the bulk of the lead precipitate.

In testing molasses of fine quality, containing but little coloring-matter, no special difficulty is encountered in carrying out these operations. On the contrary, the assay of dark low-grade materials is made very difficult by the large proportion of colored decomposition products which they contain. For example, Samples 1 and 3 of the foregoing tabulation were decolorized sufficiently for polarization in solutions of normal strength, by 1.5 cc. and 2 cc. of the writer's lead subacetate solution, corresponding to 2 cc. and 2.7 cc. of the solutions commonly employed.[1] The sugar filtrates were clear enough to be polarized with ease and great accuracy, and contained so little lead that inversion was accomplished without the slightest difficulty. On the other hand, Samples 119 and A-C were less perfectly clarified by 23-cc. portions of the writer's lead solution, corresponding to 31 cc. of the usual solutions. Only with difficulty could the filtrates from these samples be polarized accurately; and they contained so much lead that the inversion process was materially retarded by the precipitation of lead chloride, and replacement of the strongly ionized hydrochloric acid by weakly dissociated acetic acid.[2]

[1] 300 grams of lead acetate, 100 grams litharge, 1 liter of water.

[2] Samples 119 and A-C were average New Orleans third molasses,—not exceptionally black. The writer has seen specimens of the abnormal thirds mentioned in Table II which still gave dark filtrates after the addition of at least a half more basic acetate solution. Unfortunately, it was impossible to get one of these black samples for study, at the time of preparing this paper.

It has been a universal practice in the past in dealing with these very dark samples of molasses, to add a strongly basic lead solution so long as any precipitate continued to form, and if the filtrate was still too dark for convenient polarization, to continue the decolorization by using bone-black. The latter reagent has been found, however, to absorb considerable amounts of sugar, on which account its use has been discountenanced by the International Commission for Uniform Methods of Sugar Analysis.[1] Furthermore, the employment of excessive quantities and of strongly basic solutions of lead acetate has been strongly condemned during the past decade, so far as the clarification of materials containing invert sugar is concerned, on account of the danger of precipitating or isomerizing a portion of the sugar of the sample.[2]

Under these circumstances the molasses analyst may well have wondered what course he should pursue, and have determined that even an approach to accuracy is unattainable.

THE PROPOSED METHOD OF MOLASSES ANALYSIS.

Polarization in a Dilute Solution.—Many analysts who have had to work with deeply colored specimens of molasses have resorted at times to the expedient of making up the solution for polarization to something less than normal strength, instead of using bone-black and excessive amounts of lead solution; but it seems commonly to have been supposed by them that in so doing they were sacrificing accuracy to convenience. The writer is convinced, on the contrary, that the highest accuracy attainable in the polarization of dark materials is to be reached by working with comparatively weak solutions, and his own practice in most cases is to make up the normal weight of molasses—26.048 grams—to a final volume of 500 cc. Many, doubtless, to whose attention this paper may come, will be inclined to maintain that this procedure offers too great a chance for the multiplication of error. To such the answer may be returned that the process has been subjected to four years rigorous test, and that it has proved its worth, as will presently be shown.

Sources of Error in Molasses Analysis.—Before coming to a final decision regarding the merits of the procedure in question,

[1] Abstract of Proceedings, Third Session International Commission, this Journal, **23**, 59 (1901).

[2] See Pellet's numerous papers on molasses analysis, published during the last twelve years in the *Bull. de l'Ass'n des Chimistes.*

we must consider its relation to the errors which may arise from the following sources:

(1) Inaccuracy in weighing and measuring.
(2) Use of too much or too basic lead solution.
(3) Change in rotatory power of the material in solution.
(4) Faulty construction of the polariscopic apparatus.
(5) Inaccuracy in reading the saccharimeter.

Certain of these errors have been touched upon in the preceding discussion; all of them will now be considered with such added detail as may be necessary.

Errors of Weighing and Measuring.—Since it is proposed that the normal weight of molasses shall be made up to a final volume of 500 cc., and *not* that one-fifth of the normal weight shall be made up to 100 cc., it is obvious that the usual procedure and the modification now proposed stand on the same footing with reference to errors of weighing.

So far as errors of measurement are concerned, it is clear that the "fifth-normal" method—as the proposed modification will be designated throughout the remainder of this paper—possesses incontestable advantages.

In the first place, a 500-cc. flask is more likely to be calibrated accurately than is a 100-cc. flask. The internal diameter of the neck of the larger container will ordinarily be from a quarter to a half greater than that of the smaller, and the cross-section of the larger neck will be from a half larger to twice as large as that of the smaller. It follows that, equal pains being taken in calibration, the mean error per 100 cc. should be about one-third as great in a 500-cc. flask as in one containing 100 cc.[1] This fact counts, furthermore, for greater accuracy every time that a solution is made up in the larger size of flask, since the mean error of an individual filling will be only one-third as great as in the flask of the smaller size.

In the second place, every sugar analyst will recall the tenacious foam which forms in making up molasses solutions, often defying ether spray and obscuring the meniscus, and the persistence with which the thick slimy mixture retains air bubbles of considerable size, not merely in the region of the meniscus, but frequently well down in the body of the flask. These sources of annoyance, which

[1] See, in this connection, the specifications of the Committee for Coöperation with the National Bureau of Standards, this Journal, **26**, Proceedings, p. 22.

almost always appear in preparing a molasses solution of normal strength, are practically removed by working with the fifth-normal solution.

In the third place, use of the fifth-normal solution adds to the facility of analysis by giving the analyst more room to work in. Thick black molasses often requires a good deal of water for transference from the weighing-dish to the sugar flask, and it happens not infrequently that the analyst finds that he has not room enough left in a 100-cc. flask for the amount of lead solution which he needs to add. Furthermore, it is easier to remove stray drops of water from inside the neck of a large flask, and if a drop or two chance to be left the effect upon the concentration of the solution is only one-fifth as great as it would be in the small flask.

Errors Due to Lead Acetate Solution.—In discussing the customary method of analysis, reference was made to two errors arising from the use of lead acetate in clarification; and other errors were hinted at, such as the precipitation or isomerization of sugars. These errors, being of serious character, deserve further consideration in connection with the proposed fifth-normal procedure.

First, as to the error due to the bulk of the precipitate, it is obvious that it must vary as the ratio of the space occupied by the precipitate to the total volume of the mixture, or in the case of precipitates of constant bulk, inversely as the total volume of the mixture. This fact is very prettily demonstrated by certain of the writer's results.

Five of the molasses samples which were studied by the Scheibler dilution method,[1] respectively, Cuban No. 2, Cuban No. 4, 119, A-C, and McCahan, were made up in solutions of three concentrations. Of each sample, three 26-gram portions were taken; the same volume of lead subacetate solution was added to each of the three for clarification, enough being taken to decolorize the strongest solution sufficiently for accurate polarization, and the three were finally made up to the volumes of 100, 200 and 500 cc. All precautions were taken to insure the accuracy necessary in the work. The filtrates were protected from evaporation, their first portions being rejected; and before polarization they were acidified, if necessary, with acetic acid, allowance being made for any alteration of volume. Standardized flasks and polariscope tubes were used, the cover-glasses employed were free of blemishes, and previous

[1] See pp. 698 and 699.

to each series of polarization zero-point determinations were made upon each polariscope tube, fitted with its covers.[1] Constant temperature was maintained during each set of observations, at least five settings and readings were made for every zero-point or polarization, and the mean observed polarization of each solution was corrected for the minute variation in zero-point, previously determined for the tube used with that solution. The corrected observed polarizations of the half- and fifth-normal solutions were multiplied respectively by two and by five, and the values so obtained were compared with the corrected observed polarization of the normal solution for the purpose of ascertaining the true polarization of the molasses under examination. In computing the true polarizations three sets of combinations of the observed values were made, *i. e.*, $a+b$, $a+c$ and $b+c$, and the mean of the three values derived from these combinations was taken in each case as the true polarization for that sample of molasses. The results which were thus obtained are shown in the following tabulation:[2]

TABLE VII.

		Normal solution.		Half-normal solution.		Fifth-normal solution.	
Sample.	True polarization.	Observed polarization.	Error.	Observed polarization.	Error.	Observed polarization.	Error.
Cuban No. 2.	31.08	31.92	+0.84	31.50	+0.42	31.26	+0.18
Cuban No. 4.	35.24	36.20	+0.96	35.80	+0.56	35.40	+0.16
No. 119.....	16.87	17.68	+0.81	17.26	+0.39	17.03	+0.16
A–C.....	17.12	18.06	+0.94	17.60	+0.48	17.30	+0.18
McCahan ...	27.03	28.16	+1.13	27.75	+0.72	27.18	+0.15
Means.....	.....	.....	+0.94	.....	+0.51	.....	+0.17

It is clear at a glance that the use of the fifth-normal solution offers a decided advantage with regard to the magnitude of the error due to the bulk of the lead precipitate; and still another point of vantage must be mentioned which does not show in the tabulation. It has been found in the course of this study that the

[1] The writer finds it most satisfactory to use for his work the so-called "conversion tube," provided with a central aperture for the thermometer. Such tubes are readily filled and emptied through the side opening and if care is taken in rinsing, they may be used repeatedly without other cleaning.

[2] The papers of Wiechmann, and of Horne, upon the error due to the bulk of the lead precipitate, have called forth assertions from Gonnermann, Molenda, and Vermehren, to the effect that no such error is perceptible. It may be that the foregoing writers have failed to perceive it, but its existence is not to be denied on that account. When adequate precautions are taken, it is readily demonstrable.

bulks of these precipitates bear a fairly constant ratio to the amounts of lead solution used in clarification. Now, as has been said, enough of the reagent was added in all the solutions represented in the foregoing table to clarify the normal solutions thoroughly. If, as would have been the case in routine analytical work, the aim had been merely to decolorize the fifth-normal solutions sufficiently for accurate polarization, much smaller quantities of the acetate reagent would have sufficed. Thus, it has been found that Sample 119 is clarified better in fifth-normal solution by 8 cc. of the writer's lead acetate than by 22 cc. in a normal solution. Therefore, since the bulk of the lead precipitate and the error due thereto are proportional to the amount of lead solution employed, this error would be reduced to about one-third of the value given in the table, *e. g.*, to 0.05°-0.06° V. in routine analyses of such molasses.

Another argument for employing the fifth-normal procedure in molasses polarization is that we are able thereby to diminish the excess of lead which appears in the clarified solutions. The first portions of subacetate solution which are used for clarification give up most of their lead to the precipitate of coloring-matters, and comparatively little of the metal remains dissolved. As more of the reagent is added precipitation continues, but at the same time a constantly increasing proportion of the lead appears in the filtrate rather than in the precipitate. As has been said already, this accumulation of lead acetate in the normal sugar solution may at times become sufficient to interfere with inversion. The following experiment is instructive in this connection.

Two 26-gram portions of molasses Sample 119 were taken, one of which was treated with 22 cc. of basic acetate solution and made up to 100 cc., while the other received 11 cc. of the lead reagent and was made up to 500 cc.[1] The lead in the two filtrates was determined as sulphate with the following results.:

(1) *Normal Solution.*—Fifty cc. of filtrate gave 1.2370 grams lead sulphate, corresponding to 0.8530 gram lead oxide, sufficient for the neutralization of 0.2977 gram hydrochloric acid.

(2) *Fifth-normal Solution.*—Fifty cc. of filtrate gave 0.0775 gram lead sulphate, corresponding to 0.0534 gram lead oxide enough to neutralize 0.0186 gram hydrochloric acid.

[1] The filtrate from the mixture of normal concentration was about two and one-half times as strongly colored as the other, despite the fact that it had received twice the quantity of lead acetate.

Five cc. of hydrochloric acid (sp. gr. 1.19), the amount ordinarily used in inverting 50 cc. of a sugar solution, contain about 2.261 grams of HCl, and of this amount 13.2 per cent. would be neutralized by the lead salts contained in 50 cc. of the foregoing normal filtrate, whereas only 0.82 per cent. would be neutralized by an equal volume of the fifth-normal solution.

Retardation of inversion is, however, only one of the ways in which the presence of an excess of lead subacetate in a sugar solution may interfere with accurate analysis of the latter. For example, it was found some years ago by C. H. Gill[1] that the polarization of a molasses solution may be raised considerably by the addition of an excess of basic lead acetate, not merely through the formation of a bulky precipitate, but in consequence of some action of the reagent upon the sugars themselves. The increase in polarization, which is produced only in the presence of invert sugar and in an alkaline solution, is roughly proportional to the excess of lead added and is destroyed by acidification of the solution. It is believed to result from the formation, in alkaline solution, of a soluble compound of lead and levulose whose behavior toward polarized light is very different from that of levulose itself. Gill recommended the addition of sulphurous acid to the clarified solution for the purpose of destroying this compound and of restoring the polarization to its proper value; and Spencer, somewhat later, proposed the use of acetic acid for the same purpose. Still later, it was suggested by Edson[2] that a certain amount of reducing sugar is actually precipitated when basic acetate is used for clarifying cane-molasses, and it was recommended that neutral acetate be employed in its place for this purpose.[3] Still more recently, this doctrine has been advocated vigorously in France, especially by Pellet.[4]

It is not easy to decide as to the soundness of the various allegations regarding the precipitability of levulose. Edson's publication on the subject was very scanty, and his conclusions were opposed strongly by Weld[5]; and though Pellet has published many papers dealing with the question, and has cited much experimental evidence, his work is not always well planned and his arguments

[1] *J. Chem. Soc.*, April, 1871, p. 91.
[2] *J. Anal. Appl. Chem.*, **4**, 381 (1890).
[3] See also Bull. **46**, revised edition, Bureau of Chemistry, U. S. Dept. of Agr., p. 39.
[4] *Bull. de l'Ass'n des Chemistes*, **13**, 757, 836; **14**, 28, 131; **15**, 605.
[5] *J. Anal. Appl. Chem.*, **5**, 310 (1891).

are not always justified by his facts. This much may be said, however; if it *be* true that neutral or acidified lead acetate should be used in clarifying molasses for analysis, polarization in fifth-normal solutions is decidedly advantageous, for, as Pellet himself admits, the neutral acetate of lead is so poor a clarifying agent that it may fail to decolorize dark molasses far enough to permit polarization, even in a 100 mm. tube.[1] It may be said, furthermore, that there seems to be very little danger of precipitating levulose, even when a strongly basic lead solution is employed, in working at fifth-normal concentration. The writer has saved many of the precipitates obtained in the routine clarification of dark molasses, and after washing them free of soluble sugars and decomposing them with carbon dioxide and hydrogen sulphide, has tested the residues for glucoses with Fehling's solution and with phenylhydrazine. No sign of the precipitation of levulose has been observed as yet.[2]

Errors Due to Changes in Rotatory Power of Materials in Solution.—It is well understood that the specific rotatory powers of all sugars are liable to variation on a number of accounts. Changes in concentration and temperature, and the influence of other solutes which may be present in the sugar solution, are recognized to be the most important causes of variation, and the question may be raised legitimately whether any of these influences tend to favor either the usual or the "fifth-normal" procedure rather than the other.

The effect of changes of concentration upon the specific rotatory power of sucrose has been studied by many investigators, with a variety of results. Certain writers—the more important being Hesse,[3] Schmitz,[4] Tollens,[5] and Seyffart[6]—have published data which indicate that the specific rotatory power increases slightly within the limits of concentration represented by the Ventzke scale, as the proportion of sugar in the solution decreases. Tollens,[7] however, has expressed the opinion in his later papers that the specific rotation increases for a time only, as the concentration decreases,

[1] *Bull. de l'Ass'n des Chemistes*, **15**, 607 (1897).

[2] This question is being investigated in the writer's laboratory, and will be discussed fully in a later communication.

[3] *Ann. Chem.* (Liebig), **176**, 97.

[4] *Ber. chem. Ges.*, **10**, 1414 (1877).

[5] *Ibid.*, **10**, 1043.

[6] Pogg. *Ann.*, 2nd ser., **41**, 113 (1890).

[7] *Ber. chem. Ges.*, **17**, 1751.

that it reaches a maximum in the region of $C = 20$, and that it decreases from that point until it reaches the hypothetical value 66.386° at $C = 0$. Certain results obtained by Nasini and Villavecchia[1] tend to support the latter view.

Formulae have been published, giving the specific rotation in terms of the concentration, and supporting the views held respectively by Schmitz,[2] and by Tollens, and Nasini and Villavecchia.[3] With the aid of these the writer has calculated the specific rotatory powers for sucrose solutions of six concentrations, together with the Ventzke polarizations as modified by the variations in specific rotation.

TABLE VIII.

C = grams in 100 cc.	Nominal polarization.	Schmitz.		Tollens-Nasini-Villavecchia.	
		$[\alpha]_D^{20}$	Polarization.	$[\alpha]_D^{20}$	Polarization.
26.0	100.00	66.332	100.00	66.502	100.00
19.5	75.00	66.364	75.03	66.515	75.01
13.0	50.00	66.426	50.08	66.508	50.01
6.5	25.00	66.471	25.05	66.481	24.99
2.6	10.00	66.587	10.04	66.456	9.99
1.3	5.00	66.612	5.02	66.446	5.00

Although the relations of the two sets of values for $[\alpha]_D$ differ very noticeably, it will be seen that the effect of their differences upon the polarizations is very slight; too slight, indeed, to be of any consequence in the region where molasses polarizations would fall. Further evidence of this fact is afforded by the following experimental results.

Four sucrose solutions were prepared, two of which contained about 6.5 grams in 100 cc., while the others were diluted to exactly one-fifth the concentration of the first two. These solutions were polarized in a 200-mm. tube with the following results:

[1] "Sul peso normale pei saccarimetri," Rome, 1891.

[2] $[\alpha]_D^{20} = 66.639 - 0.02082\,C + 0.00034603\,C^2$ (Schmitz). "Optical Rotation of Organic Substances," Landolt-Long, p. 597.

[3] $[\alpha]_D^{20} = 66.435 + 0.00870\,C - 0.000235\,C^2$. Calculated by Landolt on the basis of observations by Tollens, and Nasini and Villavecchia, *Ibid.*, p. 465.

TABLE IX.

		Solution 1.		Solution 2.	
	Zero error.	Full strength.	Fifth strength.	Full strength.	Fifth strength.
	+0.02°	25.00°	5.00°	24.32°	4.85°
	—0.02°	24.95°	4.95	24.32°	4.88°
	—0.02°	25.05°	5.00°	24.35°	4.88°
	—0.02°	25.00°	4.95°	24.35°	4.90°
	0.00°	25.05°	5.05°	24.30°	4.90°
	0.00°	.....	5.00°	24.32°	4.88°
	+0.02°	.....	4.95°	24.32°	4.85°
	0.00°	.....	5.00°	24.35°	4.82°
	0.00°	.....	5.05°	24.35°	4.88°
	+0.02°	.....	5.00°	24.30°	4.85°
Means.	0.00°	25.01°	4.995°	24.328°	4.869°
			5		5
Mean			24.975°		24.345°
errors.	±0.005°	±0.02°	±0.065°	±0.007°	±0.040°

It is clear that the results obtained by polarizing a sucrose solution of one-fifth the usual concentration and multiplying the observed polarization by 5, agree very closely with those obtained in polarizing the solution of full strength.

The changes undergone by the specific rotatory power of invert sugar, in consequence of variation in the concentration of its solutions, have been studied by Gubbe[1] and by Ost,[2] and have been found somewhat greater than those observed for sucrose. Taking Gubbe's "concentration" formula as the basis of reckoning,[3] the writer has computed the specific rotations and the corresponding Ventzke polarizations for solutions of four concentrations within the range of the amounts contained in molasses.

TABLE X.

Concentration.	$[\alpha]_D^{20}$	Polarization.
8.421	—19.961	—9.70
4.210	—19.809	—4.81
1.684	—19.718	—1.92
0.842	—19.687	—0.96

With the aid of these figures it is possible to calculate the effect of alterations in concentration on the polarization of molasses

[1] *Ber. chem Ges.*, **18**, 2207.

[2] *Ibid.*, **24**, 1636.

[3] $[\alpha]_D^{20} = -19.657 - 0.0361\ C$. "Optical Rotation of Organic Substances," Landolt. Long, p. 592.

solutions. For the purpose of this computation we may assume the following data:

TABLE XI.

	High-grade molasses.		Low-grade molasses.	
	Sucrose.	Invert sugar.	Sucrose.	Invert sugar.
Sugar percentages.....	50.00	16.20	25.00	32.40
Concentration in normal solution	13.00	4.21	6.50	8.42
Concentration in fifth-normal "	2.60	0.84	1.30	1.68

Taking the sucrose polarizations given in Table VIII and calculated on the basis of the Schmitz formula, we have the following results:

TABLE XII.

	High-grade molasses.		Low-grade molasses.	
	Normal.	Fifth normal.	Normal.	Fifth-normal.
Sucrose polarization.....	50.08°	10.04	25.05°	5.02°
Invert sugar polarization.....	—4.81°	—0.96°	—9.70°	—1.92°
Direct polarization.....	45.27°	9.08°	15.35°	3.10°
		5		5
		45.40°		15.50°
Fifth-normal result high, by		0.13°		0.15°

With regard to the changes of specific rotatory power which would arise from making up and polarizing molasses solutions at some other temperature than the standard one of 20° C., it is impossible to see that there would be any choice between the use of solutions of normal or fifth-normal strength.

The influence of the non-saccharine materials present in molasses solutions upon the optical activity of the sugars has not been studied in connection with the proposed procedure. All that can be said at present is that the polarizations of normal molasses filtrates which have been diluted exactly five times compare with the original polarizations as follows:

TABLE XIII.

		Second molasses.		Third molasses.	
	Zero error.	Full strength.	Fifth strength.	Full strength.	Fifth strength.
	+0.02°	25.25°	5.10°	18.45°	3.82°
	0.08°	25.20°	5.15°	17.90	3.75°
	0.05°	25.32	5.15°	18.55°	3.75°
	0.02°	25.25°	5.10°	18.10°	3.72°
	0.08°	25.22°	5.12°	18.60°	3.78°
	0.05°	25.25°	5.15°	17.85°	3.72°
	0.05°	25.32°	5.10°	18.30°	3.75°
	0.05°	25.28°	5.15°	18.20°	3.75°
	0.05°	25.30°	5.15°	18.35°	3.72°
	0.05°	25.20°	5.12°	18.15°	3.72°
Means...	+0.05°	25.254°	5.129°	18.25°	3.748°
		—0.05°	—0.05°	—0.05°	—0.05°
Corrected means		25.20°	5.079°	18.20°	3.698°
			5		5
Fifth-strength polarizations × 5			25.39°		18.49°
Fifth-strength results, high by			0.19°		0.29°

It is interesting to notice that these experimental results confirm the prediction of Table XII to the effect that polarizations obtained by use of the fifth-normal solution will be slightly higher, for mixtures of sucrose and invert sugar, than the direct polarizations of normal solutions, when there is no "lead precipitate" error to be reckoned with.

In connection with the subject of specific rotation, it should be said that the factor to be used as a divisor in the Clerget equation deserves further study with relation to the problem of molasses analysis. It has been shown by Herzfeld[1] to vary according to the concentration of sucrose in the solution to be inverted, and it is known also to vary according to the concentration of the hydrochloric acid in such a solution.[2] Furthermore, as Tolman[3] pointed out a few years ago, it varies according to the amount of invert sugar which is present together with sucrose in the material under examination. The writer is using at present the value 142, having found that the results thus obtained agree well with those obtained by determining sucrose in the chemical way, but he pro-

[1] Stammer's Jahresber, 1890, p. 142.
[2] Lippmann : *Chemie der Zuckerarten* (2nd Edition), p. 800.
[3] This JOURNAL, **24**, 515 (1902); *Bull.* **73**, Bureau of Chem., U. S. Dept. of Agr., p. 75.

poses to investigate the question of this factor at the first opportunity.

Errors Due to Faulty Apparatus and Observation.—The sources of error which already have been discussed have been shown either to favor employment of the "fifth-normal" procedure or to be so slight that the danger of multiplication need not be feared. The errors which now remain to be considered are on the contrary of a more threatening character, since they never can be wholly eliminated and are certain, almost without exception, to be multiplied by 5 in working with fifth-normal sugar solutions. They demand, therefore, serious and detailed consideration, for which there is too little space in the present communication. They will be discussed fully in a paper now in course of preparation upon the graduation of Ventzke saccharimeters and the degree of precision attainable in their employment, and for the moment they can be referred to only in the briefest fashion.

The writer and several of his acquaintances, whose saccharimeters are provided with good scales and verniers, have found it easy to read the scale to about one-quarter of a tenth degree, *i. e.*, to about 0.02°–0.03° V. Furthermore, when the optical parts of the saccharimeter are in good order and the illumination is properly controlled, movement of the wedge through 0.05° will produce a change in the field in the vicinity of the zero-point, which is detected readily by the eye of a practiced observer. When a number of observations are made with proper care, the eye being rested between them, they will be found to differ very slightly and the mean error of their average value will be very small indeed. Evidence of this is given in the errors shown in Table IX.

It is to be understood, of course, that the mean error of a polarization includes in addition to the error of the polarization itself, the error of a zero-point determination taken at the same time. The sum of these mean observation errors should not be more than about ±0.03° V.[1] when quartz plates or fairly colorless solutions are being polarized. If, however, it is attempted to work with dark solutions the magnitude of the error increases rapidly. Thus, the mean error of the value 25.20°, given in Table XIII as the polarization of a full-strength solution of second molasses, is ±0.025° V., whereas the error of the corresponding value of 18.20°

[1] Compare Schönrock's statement, in "Optical Rotation of Optical Solutions," Landolt-Long, p. 388.

given for the third molasses is about $\pm 0.09°$, the latter solution having been about twice as dark as the former.

With such clear solutions as are readily obtainable through use of the fifth-normal procedure the observation error should be kept down to $\pm 0.03°$, and in multiplying the observed polarization by 5, to compensate for the dilution of the solution, the error will also be multiplied and will become $\pm 0.15°$, which is less than would be obtained ordinarily in polarizing dark solutions of normal strength.

That the degree of precision just described is attainable in routine every-day work has been shown to the writer's satisfaction by the experience of himself and certain of his acquaintances during the past two years; but it is not attainable unless suitable precautions are taken. Faulty illumination, flaws in the prisms or wedges, optically active cover glasses, observation tubes whose ends are not cut in planes perpendicular to their axes, illy divided or corroded scales—all may be responsible for errors far greater than those which have been discussed. It is a part of the analyst's business, however, to know his tools and to guard against errors of this sort.

CONCLUSION.

We now have seen that the errors which may arise in weighing and measuring are likely to favor adoption of the fifth-normal procedure; that those due in one way or another to the use of lead acetate in clarification are decidedly in its favor; that there is little choice between the usual and the proposed procedures so far as the influence of specific rotation is concerned; and finally, that with care the use of fifth-normal solutions for polarization may diminish the observation error in the assay of dark molasses, although without care the opportunity for such error is unquestionably increased.

Of course, no claim is made that precision is attainable by adoption of this procedure; but after four years of routine test in factory analysis and two of careful critical study the writer is convinced that its use has opened the way to an advance in accuracy.

FROM THE LABORATORY OF FELTON AND SON,
BOSTON, MASS.

GASOMETRIC DETERMINATION OF FORMALDEHYDE.

By G. B. Frankforter and Rodney West.

Received April 10, 1905.

In studying the reaction which takes place when formaldehyde is brought in contact with potassium permanganate, it became necessary to know the exact amount of aldehyde expelled by the heat of combustion, together with the amount of carbon dioxide and formic acid, in order to determine the amount of aldehyde actually oxidized by the permanganate. To make these determinations as accurate as possible, various methods for the determination of formaldehyde were tried. In addition to the difficulties experienced in determining formaldehyde in the presence of formic acid and carbon dioxide, we were surprised to find that the common methods, which are regarded as accurate, would not check on all samples which we examined. Some of these methods gave comparatively concordant results with certain samples of aldehyde, while other methods gave results which varied as widely as 3 per cent. It therefore became necessary to find some quick method which would give as correct results as possible and at the same time be convenient as well as rapid in our calorimetric determination.

To obtain these results the common methods of determining formaldehyde were compared with each other. We began by trying the common ammonia method and its modified form by Smith,[1] together with the hexamethylene and the old alkaline method of heating the aldehyde with potassium hydroxide in pressure flasks. Finally, we studied the reaction mentioned by Blank and Finkenbeiner,[2] in which hydrogen peroxide is used together with an alkali. In examining the last-mentioned it was found that hydrogen in a pure state is liberated. It therefore occurred to us that perhaps this fact would afford a rapid, and at the same time an accurate, method of determining formaldehyde, gasometrically, in the presence of formic and carbonic acids.

When formaldehyde is brought in contact with a solution of sodium or potassium hydroxide a reaction takes place resulting in oxidation on the one hand, and reduction on the other, according to the well-known reaction:

$$2CH_2O + KOH = HCOOK + CH_3OH.$$

[1] *Am. J. Pharm.*, **70**, 86.

[2] *Ber.*, **31**, 2979.

When, however, these two substances are brought together in the presence of hydrogen peroxide the reaction is changed, notwithstanding the fact that both oxidation and reduction take place. As above, potassium formate is formed, but in place of methyl alcohol, pure hydrogen is liberated, according to the following equation:

$$2CH_2O + 2KOH = 2HCOOK + 2H_2O + H_2.$$

One molecule of hydrogen is liberated for every two molecules of formaldehyde. A study of this reaction showed that the hydroxides of practically all of the light metals would liberate hydrogen in the presence of hydrogen peroxide, while the peroxides of the same metals would liberate hydrogen without the addition of hydrogen peroxide. The peroxides of the alkali metals produce an explosion when brought in contact with strong formaldehyde; if diluted with water, an energetic reaction takes place, liberating

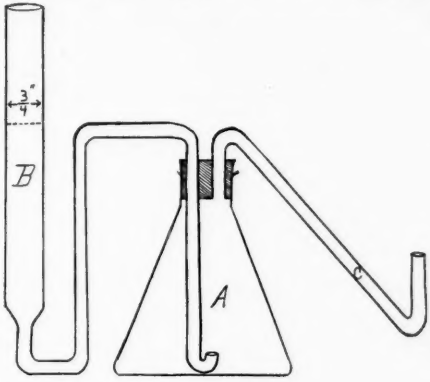


Fig. 1.

hydrogen, and when the reaction is too violent a small quantity of oxygen is liberated. In the same way the peroxides of the alkali earths act upon formaldehyde, but hydrogen is liberated very slowly without the addition of free hydrogen peroxide.

It first became necessary to test the purity of the hydrogen. For this purpose a special generator[1] was used. It consisted of an Erlenmeyer flask, A (Fig. 1), fitted with a double-bored cork.

[1] This apparatus will be fully described later by one of us and Mr. Francis Frary under New Lecture Apparatus (see this JOURNAL, **27**, 746). We have used this piece of apparatus very successfully in determining the hydrogen equivalent of zinc.

Through one hole is passed a funnel tube, *B*, the funnel part being a wide tube which prevents air bubbles from passing over into the generator when the reagent is added. A common delivery tube, *C*, is inserted in the other hole of the cork. The flask is filled with water free from air, and a few cubic centimeters each of formaldehyde and hydrogen peroxide are added. When the generator, including the delivery tube, is completely filled, a solution of potassium hydroxide is poured into the funnel. It passes over into the flask and there comes in contact with the aldehyde and the peroxide. Hydrogen is liberated and can readily be collected without containing even a trace of air. In our first determinations, distilled water, which had stood in the air for some time, was used both in the generator and in the gasometer. Several analyses gave 99.7 per cent. pure hydrogen. Later, water free from air was used, in which case the hydrogen proved to be chemically pure.

DETERMINATION.

Several different forms of apparatus were tried in determining the quantity of hydrogen liberated. The Scheibler-Finkner calcimeter, with a graduated tube of 300 cc. capacity, was finally selected as giving best results. The generator bottle used was one with a side tube, so that it could be shaken vigorously without danger of breaking. A pressure-bottle with a stop-cock was also tried in order to determine whether or not any aldehyde was carried over with the hydrogen.

For rapid work 1 cc. of aldehyde of known specific gravity was used, although good results were obtained with half that amount. The aldehyde is placed in the side tube of the generator, and 10 cc. of hydrogen peroxide and 20 cc. of normal potassium hydroxide are placed in the body of the generator. The generator is closed and the water in the measuring tube is brought to zero. After the temperature has become constant a small quantity of the mixture of peroxide and hydroxide is allowed to come in contact with the formaldehyde. Hydrogen is rapidly liberated with evolution of considerable heat. When the reaction is completed the apparatus is allowed to stand until the generator bottle has again reached the room temperature, when the volume of hydrogen is read off. With the corrected volume of gas it is a very simple matter to calculate the per cent. of formaldehyde. The exactness of the equation was proved by beginning with samples of known strength.

In making these comparisons it was found that when a large amount of hydrogen peroxide and strong potassium hydroxide were used the results obtained were a little higher than those obtained by the other methods. After experimenting with the strength of these reagents, we found that when 1 cc. of aldehyde was used with 10 cc. of hydrogen peroxide and 20 cc. of normal potassium hydroxide the results obtained checked very closely with other methods. The following table gives comparative results on the same samples:

	Method.			
Sample.	Hexamethylene.	Ammonia.	Alkali.	Gasometric.
D	37.76	37.89	38.16	38.26
"	37.70	37.90	38.09	38.16
"	37.58	38.04	38.16	38.16
"	37.66	37.81	38.28	38.60
"	33.26	33.35	33.82	34.00
F	33.12	33.62	33.77	34.20
"	33.62	33.52	33.91	33.96
"	33.09	33.32	33.88	34.00

In the above analyses the same amount of peroxide and the same amount of hydroxide were used, namely, 10 cc. peroxide and 20 cc. of normal potassium hydroxide with 25 cc. of distilled water.

THE USE OF SODIUM PEROXIDE INSTEAD OF HYDROGEN PEROXIDE.

It was found that sodium peroxide gave, with formaldehyde, the same peculiar reaction which hydrogen peroxide gives. When the aldehyde comes in contact with sodium peroxide, unless the aldehyde is considerably diluted, the reaction is exceptionally violent and now and then results in an explosion. If the peroxide is first cautiously dissolved in water so as to liberate little or no oxygen, and then brought in contact with formaldehyde, hydrogen is liberated according to the following equation:

$$2CH_2O + Na_2O_2 = 2HCOONa + H_2.$$

The best results were obtained by using 2 grams of peroxide dissolved in 50 cc. of water with 1 cc. of aldehyde.

The results obtained with sodium peroxide were a little higher than by the use of hydrogen peroxide, more than likely due to the liberation of oxygen on bringing sodium peroxide in contact with water. An average of five analyses with sodium peroxide was 36.29 per cent. of formaldehyde, while the average of the same number of analyses with hydrogen peroxide was 35.88 per cent.

We are sure however that physical conditions are largely the cause of the varying results.

In studying the results it occurred to us that perhaps a trace of alcohol or formic acid might account for the high results. Analyses were therefore made introducing both methyl alcohol and formic acid besides the aldehyde. In each case the results were slightly less, instead of more, as would be expected. The following analyses will give a comparison.

In all these analyses, 2 grams of sodium peroxide, 1 cc. of formaldehyde of known specific gravity with 50 cc. of water were taken. To this was added 1 cc. of methyl alcohol and 1 cc. of formic acid. Results of these analyses are given below:

Per cent. of aldehyde		
without alcohol or acid.	with alcohol.	with formic acid.
37.08	35.51	35.79
36.64	35.78	35.86
36.07	35.78	35.92
35.92	35.70	35.64

Similar results were obtained with hydrogen peroxide in the presence of methyl alcohol and formic acid, that is, lower results in the presence of methyl alcohol than in either of the other cases. A probable explanation is that part of the oxidizing reagent was used in converting the alcohol to formic acid. It was found that alcohol was slowly oxidized to formic acid. A large number of determinations were made with varying amounts of hydrogen peroxide. It was found that with an excess of peroxide the results checked well with those made in the absence of methyl alcohol. The following table will verify this statement:

Per cent. of aldehyde		
without alcohol or acid.	with alcohol.	with formic acid.
33.28	33.28	33.42
33.50	33.28	33.31

In these analyses proportions of 40 cc. of normal potassium hydroxide, 20 cc. of hydrogen peroxide and 1 cc. of formaldehyde of known specific gravity were taken.

THE ACTION OF BARIUM PEROXIDE ON FORMALDEHYDE.

Barium peroxide, in the presence of water, slowly acts upon formaldehyde, liberating hydrogen. In the cold the reaction is

very slow and incomplete. When heated, a quantitative reaction seems to take place:

$$4CH_2O + Ba_2O_2 = 2(CHO_2)Ba + 2H_2.$$

The reaction takes place more readily in the presence of free hydrogen peroxide. The results, however, were lower than with sodium peroxide. An average of five analyses with sodium peroxide gave 34.88 per cent. of formaldehyde, while with barium peroxide and hydrogen peroxide an average of 32.9 per cent. was obtained.

THE ACTION OF MANGANESE AND LEAD PEROXIDES ON FORMALDEHYDE.

The dioxides of manganese and lead are practically inert with formaldehyde alone. If hydrogen peroxide is added, as in the case of barium peroxide, oxygen, instead of hydrogen, is liberated. The amount of oxygen seems to be entirely independent of the presence of formaldehyde. The reaction seems however to be more vigorous in the presence of formaldehyde. Further examination is being made.

That the reaction which takes place between formaldehyde and hydrogen peroxide in alkaline solution is quantitative, there can be no doubt. Several things must be taken into consideration, however, in order that accurate results may be obtained. Special attention must be given to temperature, as considerable heat is generated in the reaction. The quantities of the reagents also vary the results. Large amounts of hydrogen peroxide and potassium hydroxide give higher results than moderate amounts of the reagents. This may be remedied, however, by diluting the reagents.

With proper care in manipulation very concordant results may be obtained, and the presence of formic acid, methyl alcohol and other impurities do not interfere or change results.

UNIVERSITY OF MINNESOTA.

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

THE DETERMINATION OF VANILLIN, COUMARIN AND ACETANILIDE IN VANILLA EXTRACT.

BY A. L. WINTON AND E. MONROE BAILEY.

THE Hess and Prescott method[1] for the determination of vanillin and coumarin soon after its appearance, was adopted as a

[1] This Journal, **21**, 256 (1899).

provisional method by the Association of Official Agricultural Chemists, and has come into general use in American food laboratories. Winton and Silverman[1], working with extracts made in the laboratory from pure vanillin and coumarin, found that this method, slightly modified, gave remarkably accurate results for vanillin, and reasonably accurate results for coumarin. When, however, as high as 0.30 per cent. of coumarin was present, there was a deficiency of 5 to 10 mg., equivalent to 0.02 to 0.04 per cent. of the extract.

This slight loss of coumarin, we have since found, was sustained during de-alcoholizing, and may be largely or entirely obviated by following the instructions given on page 722, thus avoiding over-concentration. The loss of coumarin from a concentrated solution is so great as to render the analysis entirely worthless. For example, in evaporating 25 cc. of an extract containing 0.30 per cent. of coumarin three times to a volume of 10 cc., this loss amounted to over half the total quantity present.

Adulteration of Vanillin with Acetanilide.—In a circular, issued by a well-known chemical house in 1901, attention was called to low-priced vanillin then on the market, sold usually under foreign labels, which, according to analysis, was adulterated with 35 per cent. of acetanilide. It was further stated that this practice was not only dishonest, but a menace to health, and that the house would analyze free of charge suspected samples.

None of the commercial vanilla extracts analyzed at this Station, during the year 1901, contained acetanilide, although many of them were unquestionably made from synthetic vanillin, but during the present year 4 out of 47 adulterated extracts examined, contained amounts ranging from 0.08 to 0.15 per cent. The percentages of vanillin, coumarin and acetanilide in these samples, and the melting-points of the acetanilide, were as follows:

DETERMINATIONS OF VANILLIN, COUMARIN AND ACETANILIDE IN COMMERCIAL VANILLA EXTRACTS.

Serial number.	Vanillin. Per cent.	Coumarin. Per cent.	Acetanilide. Per cent.	Melting-point of acetanilide. Degrees C.
12806	0.35	0.06	0.13	113
12903	0.21	0.04	0.08	113
12907	0.31	0.00	0.13	112
12911	0.19	0.00	0.15	112

[1] This Journal, **24**, 1128 (1902).

These results indicate that these extracts were made from vanillin containing from 27 to 45 per cent. of acetanilide.

Detection of Acetanilide.—This adulterant is readily detected in the course of Hess and Prescott's process by the incomplete solubility in petroleum ether of the residue, which in the case of extracts free from acetanilide is pure coumarin, by the melting-point of the insoluble portion (112° C.), and by its qualitative reactions. The weighed residue of coumarin and acetanilide is stirred for fifteen minutes with 15 cc. of petroleum ether, the clear solution is carefully decanted, and the operation of stirring and decanting is repeated three times. This we have found sufficient in all cases for complete solution of the coumarin without dissolving appreciably the acetanilide.

The residual acetanilide is dried in a desiccator, weighed, and tested as to its melting-point and reactions. The weight deducted from the weight before dissolving out the coumarin, gives the weight of the coumarin. The extract is allowed to evaporate at room temperature, and the melting-point of the crystals determined. If desired, the coumarin can be weighed, but it is more accurate and convenient to obtain this ingredient by difference.

We have found the following qualitative reactions recommended by Ritsert,[1] to be reliable:

Boil the residue in a small beaker for two or three minutes with 2 to 3 cc. of concentrated hydrochloric acid, cool, divide into three portions, and test in small tubes (4 to 5 mm. inside diameter) as follows:

(1) Indophenol reaction. To one portion add carefully 1 to 3 drops of a solution of chlorinated lime (1 : 200) in such a manner that the two solutions do not mix. A beautiful blue color formed at the juncture of the two liquids indicates acetanilide.

(2) To another portion add a small drop of permanganate solution. A clear, green color is formed, if any appreciable amount of acetanilide is present.

(3) Mix the third portion with a small drop of 3 per cent. chromic acid solution. Acetanilide gives a yellow-green solution, changing to dark green on standing five minutes, and with the formation of a dark blue precipitate on addition of a drop of caustic potash solution.

We have not found the indophenol test adopted by the German

[1] *Pharm. Ztg.*, **33**, 383; Abs. *Z. anal. Chem.*, **27**, 667 (1888).

Association of Pharmacists[1] so satisfactory as Ritsert's modification, as blank tests often give a blue color, due probably to impurities in the phenol employed.

Method of Determining Vanillin, Coumarin and Acetanilide.—The following modification of the Hess and Prescott method gives satisfactory results for all three substances:

Weigh out 25 grams into a 200 cc. beaker with marks showing volumes of 25 and 50 cc. Dilute to the 50 cc. mark, and evaporate in a water-bath to 25 cc. at a temperature in the bath of not more than 70° C. Dilute a second time to 50 cc., and evaporate to 25 cc. Add normal lead acetate solution drop by drop until no more precipitate forms. Stir with a glass rod to facilitate flocculation of the precipitate, filter through a moistened filter, and wash three times with hot water, taking care that the total filtrate does not measure more than 50 cc. Cool the filtrate, and shake with 20 cc. of ether in a separatory funnel. Remove the ether to another separatory funnel, and repeat the shaking of the aqueous liquid with ether three times, using 15 cc. each time. Shake the combined ether solutions four or five times with 2 per cent. ammonia, using 10 cc. for the first shaking, and 5 cc. for each subsequent shaking. Set aside the combined ammoniacal solutions for the determination of vanillin.

Wash the ether solution into a weighed dish, and allow the ether to evaporate at the room temperature. Dry in a desiccator, and weigh. Stir the residue for fifteen minutes with 15 cc. of petroleum ether (boiling-point 30° to 40° C.), and decant off the clear liquid into a beaker. Repeat the extraction with petroleum ether two or three times. Allow the residue to stand in the air until apparently dry, completing the drying in a desiccator. Weigh, and deduct the weight from the weight of the residue obtained after the ether evaporation, thus obtaining the weight of the coumarin. This residue, if acetanilide, should have a melting-point of about 112° C., and respond to the qualitative tests already given.

Allow the petroleum ether extract to evaporate at room temperature. If it is pure coumarin, it should have a melting-point within a few degrees of 67° C., and respond to Leach's test.[2]

Slightly acidulate the ammoniacal solution, reserved for vanillin, with 10 per cent. hydrochloric acid. Cool, and shake out in

[1] *Z. anal. Chem.*, **27**, 666 (1888).

[2] "Food Inspection and Analysis," p. 732.

a separatory funnel with four portions of ether, as described for the first ether extraction. Evaporate the ether at room temperature in a weighed platinum dish, dry over sulphuric acid, and weigh.

If acetanilide has not been previously detected, this residue should be pure vanillin, with a melting-point within a few degrees of 80° C.

If acetanilide has been detected, dissolve the residue in 15 cc. of 10 per cent. ammonia, and shake out twice with an equal volume of ether. Evaporate the ether solution at room temperature, dry in a desiccator, and weigh. Deduct this weight from the previous weight, thus obtaining the weight of pure vanillin. The total weight of the acetanilide is obtained by adding the weight of this last extract to that of the residue previously obtained, and identified as acetanilide.

In doubtful cases the ammoniacal solution should be acidified, shaken out with ether, and the melting-point of the vanillin, obtained by evaporation at room temperature, determined.

It is quite possible that the first shaking with ammonia would effect a complete separation of vanillin from both coumarin and acetanilide, if a smaller amount of ammonia of greater strength were used, as first proposed by Hess and Prescott. We have found, however, that the more dilute ammonia is much more satisfactory for ordinary extracts free from acetanilide, and it seems, therefore, undesirable to modify the process to fit exceptional samples.

Test Analyses.—In order to test the accuracy of the above-described process, an extract was prepared in the laboratory containing 20 per cent. of cane-sugar, 40 per cent. of alcohol, and in each 25 cc., 0.0750 gram each of pure vanillin, coumarin and acetanilide. The results obtained on six 25-cc. portions of this extract are given in the following table:

ANALYSES OF AN ARTIFICIAL VANILLA EXTRACT CONTAINING KNOWN AMOUNTS OF VANILLIN, COUMARIN AND ACETANILIDE.

	I. Gram.	II. Gram	III. Gram.	IV. Gram.	V. Gram.	VI. Gram.	Taken. Gram.
Weight of residue containing coumarin and acetanilide	0.1305	0.1250	0.1272	0.1262	0.1283	0.1278	
Weight of acetanilide	0.0553	0.0535	0.0559	0.0555	0.0551	0.0555	

	I. Gram.	II. Gram.	III. Gram.	IV. Gram.	V. Gram.	VI. Gram.	Taken. Gram.
Total weight of coumarin (by difference)	0.0752	0.0715	0.0713	0.0707	0.0732	0.0723	0.0750
Weight of residue containing vanillin and acetanilide	0.0928	0.0917	0.0906	0.0908	0.0900	0.0922	
Weight of acetanilide	0.0216	0.0192	0.0145	0.0168	0.0156	0.0161	
Total weight of vanillin (by difference)	0.0712	0.0725	0.0761	0.0740	0.0744	0.0761	0.0750
Total weight of acetanilide	0.0769	0.0727	0.0704	0.0723	0.0707	0.0716	0.0750

The purity of the coumarin, vanillin and acetanilide as weighed out, also as recovered in the course of the analyses, was established by determination of melting-points.

The amounts of the three substances used were in each case 0.0750 gram, equivalent to about 0.3 per cent. of the extract. The error in the determination of each in no case reached 0.0050 gram, equivalent to about 0.02 per cent.

[Contribution from the Leather and Paper Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.
Sent by H. W. Wiley.]

THE EXTRACTION OF TANNING MATERIALS WITH VARIOUS EXTRACTORS.[1]

By F. P. Veitch.

Received March 18, 1905.

Owing to the fear that tannin may be oxidized by prolonged boiling, and to the fact that the extraction of certain materials gives maximum results only at low temperatures, a number of forms of apparatus have been used for the laboratory extraction of tanning materials. At present, however, but two extractors are in general use: the Koch or some modification of it, as that of Proctor, and a modified Soxhlet, devised at the Vienna Research Laboratory, and generally known as the Weiss extractor.

There are several objections to each of these extractors. With the Koch extractor, the evaporation of the extract, which amounts to 2 to 4 liters, is a decidedly objectionable feature, requiring considerable time, and encouraging to a certain extent, the very thing it was designed to prevent, namely, the oxidation of the

[1] Read before the Association of Official Agricultural Chemists, St. Louis, October 1904.

tannins by boiling. In addition, there is reason to believe that where the tanning material is put in the extractor dry, the most convenient way, there is often some channelling, and the extraction is incomplete, as illustrated in the case of the spent hemlock bark given in the table. On the other hand, the Koch apparatus enables one to control the temperature of extraction as no other form now in use does, and for this reason, especially, has its use seemed to be advisable with materials high in starch. Notwithstanding the fact that Eitner *et al.*,[1] found that the Weiss extractor gave satisfactory results, tanning chemists have generally looked with misgiving on it, fearing oxidation during the long-continued boiling of the strong extract. Indeed, Palmer,[2] Procter and Parker,[3] and Parker[4] have found that from many materials less tannin is extracted at boiling than at a lower temperature. The total volume of extract in these experiments was only 1 liter, however, and it seems possible that longer extraction would have given more tannin at the higher temperatures.

The International Association of Leather Trades Chemists has adopted the Koch (or Procter) extractor as official, and Procter[5] regards the prolonged boiling of the extracted materials, such as takes place in the Weiss extractor, as inadmissible.

On the other hand, in addition to Eitner *et al.*, Bough[6] has found that the Weiss extractor gave higher results than the Koch extractor on oak, and pine bark, valonia, sumac, and Quebracho wood, and gave lower results on divi-divi and Myrobalans. The Weiss extractor is used in most tannery laboratories in this country in extracting woods and barks.

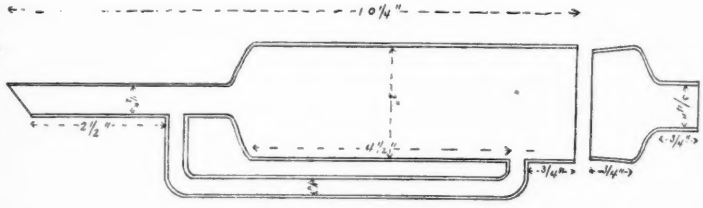
It will thus seem that there is considerable difference of opinion as to the accuracy of the results and the losses of tannin obtained with these two methods of extraction. I have, therefore, endeavored to avoid the difficulties and objections presented by these generally used methods, by substituting an extractor with which the evaporation and concentration of large volumes of dilute liquors, obtained by the Koch method, is avoided, and with which the prolonged boiling of the gradually strengthening extract and its frequent concentration and dilution, as with the

[1] Der Gerber, 1887, p. 3.
[2] See Procter's "Principles of Leather Manufacture," p. 344.
[3] *Jour. Soc. Chem. Ind.*, **14**, 635.
[4] *Ibid.*, **17**, 106 (1898).
[5] Vide "Leather Industries Laboratory Book, and Principles of Leather Manufacture."
[6] Abstract *J. Soc. Chem. Ind.*, **18**, 303 (1899).

Weiss, is not necessary. Such an extractor is found in the old and well-known double tube continuous extractor, or in the side tube extractor devised by Zulkowsky. With the former, the extraction takes place at 95°-100° C., with the latter at 90°-95°. Undue concentration and boiling of the extract is avoided by placing only about 250 cc. of water in the receiving flask, and after the extraction has continued a short time, replacing the receiving flask by another containing the same amount of water. This is repeated at longer intervals, until the extraction is completed, the total volume of extract being kept within a liter.

When it is desired to extract the first portions at temperatures below boiling, it is only necessary to allow water of the given temperature to flow slowly into the filled extractor, and to continue the percolation until 500 cc. of extract have been obtained. Water is then placed in the receiving flask, and the extraction finished at steam heat.

The extractor is sufficiently described in the accompanying drawing. The extractor may be made of glass or tinned copper. When glass is used, it should be of such a character as not to yield appreciable quantities of alkalies to steam on prolonged boiling, as the soluble solids are affected thereby. It is difficult to get a side tube extractor of glass that will stand a temperature of 100° C., so that copper extractors are most satisfactory.



In loading the extraction tube a perforated porcelain disk is first placed in it, and the weighed material, previously mixed with water to a thin paste, is washed into the extractor, and gently pressed down in order to make it fairly firm. Another perforated porcelain disk is placed on top of the material. The cloudy extract, which has passed through into the receiving flask, is returned to the extractor, which is then connected with the condenser. The perforated disk on top of the material distributes the con-

densed water, and is prevented from rising above the entrance of the side tube by coming in contact with the end of the condenser tube, which should come down to this point. This prevents escape and loss of material, which is apt to be caused by the expansion of the air and steam in finely ground materials. Wetting the material before putting it in the extractor prevents channelling, and insures regular extraction.

Comparative results, which have been obtained with all three forms of extractor, are given in the table. The time of extraction was the same with all extractors, and it was found necessary to continue it for two working days, or about fifteen hours with the Koch extractor, when extraction was discontinued with all.

The results marked (1) were obtained with the Weiss, (2) with the Koch, and (3) with the continuous extractor. The samples include the most generally used native tanning materials, except chestnut and oak bark.

RESULTS OBTAINED WITH DIFFERENT EXTRACTORS.

Material.	Extractor.	Total extract. Percent.	Soluble solids. Percent.	Reds. Percent.	Non-tannin. Percent.	Tannin. Percent.
Bark of Tan bark oak.....	1	27.04	26.06	0.98		
	2	27.38	26.82	0.56	10.60	16.22
	3	29.66	28.68	0.98		
Bark of Tan bark oak "rump bark"	1	45.76	43.72	2.04		
	2	44.92	42.06	1.86	12.86	19.20
	3	47.64	45.48	2.16		
Pecan shells.....	1	12.72	12.08	0.64		
	2	11.36	.....	....	1.73	9.63
	3	13.24	12.52	0.72		
Hemlock bark new	1	18.47	16.10	2.17		
	2	17.43	15.63	1.80	4.75	10.88
	3	23.10	19.37	3.73	7.48	11 89
Hemlock bark, spent	1	.....	.....	....	.....	.....
	2	3.06	2.93	0.13	1.57	1.36
	3	8.29	7.24	1.05		
Chestnut wood.....	1	13.68	12.28	1.40	4.75	7.43
	2	8.98	8.53	0.40	2.25	5.28
	3	12.50	11.20	1.30	3.63	7.57
Sumac leaves, course ground.	1	52.05	49.70	2.35	28.54	21.16
	2	47.42	45.72	1.70	20.74	24.98
	3	53.57	49.85	3.72	27.29	22.56
" " fine ground...	3	53.12	49.70	3.42	25.92	23.78

In examining the results, total extract may be omitted from consideration, as this determination often includes some of the material, which was mechanically carried over into the extract. This is particularly true with the results from the Weiss extractor. Although the solid material was given time to settle before drawing out for total solids, not much importance is attached to figures for total extract.

The figures show how radically the results may differ under different conditions of extraction.

Soluble solids were highest by the continuous extractor, except in the case of chestnut wood, where I believe the coarseness of the sample was in favor of the Weiss extractor. The Weiss extractor gives higher results than the Koch extractor, except on one sample of Tan Oak bark. Tannin is highest with the continuous extractor, except with sumac, where, notwithstanding the lowest soluble solids, tannin is the highest, when the Koch extractor was used.

As a rule, it appears that where the extraction is continued for some time, all constituents, reds, non-tannin, and tannin, are removed in somewhat larger quantities by using a continuous extractor. Except in the case of sumac, there is nothing to indicate that there is any serious loss of tannin, or, perhaps we should say, any material difference in the loss of tannin from any cause, with any of the extractors. While reds and non-tannin are usually higher when the continuous extractor is used, this fact, in the face of high tannin, is not conclusive evidence, that any loss of tannin has occurred. As has been said, apparently larger amounts of all soluble constituents have been dissolved.

The conflicting results obtained from the different investigations on the effect of heat on the extraction of tannin and on its oxidation, renders further investigation very desirable. I am convinced, that the chief explanation of these conflicting results is to be found in imperfect extraction, due to the small quantity of water usually passed through the Koch apparatus, and to too few siphonings with the Weiss. Procter and Parker in their investigation of the effect of temperature used only one liter of water, and text-books generally give one to understand that complete extraction may be secured with two liters or less of water. My experience leads me to doubt this very much, as I usually find

tannin being removed in considerable quantities, after extracting with three or four liters during eight to twelve hours.

This investigation will be continued, and extended to include other tanning materials.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

DETERMINATION OF SULPHUR AND PHOSPHORIC ACID IN FOODS, FECES AND URINE.

BY W. L. DUBOIS.

Received March 20, 1905.

IN a previous contribution[1] from the Bureau of Chemistry, the methods then in use for the determination of sulphur and phosphoric acid in connection with the metabolism experiments being conducted by Dr. Wiley and Dr. Bigelow were described. Since the appearance of that article, some important changes in the method of burning foods and feces have been made, to which I wish to call attention. Urines are still burned by Osborne's method, the facility of handling them in that way being all that could be desired. In this work all phosphoric acid determinations were made by Mr. C. W. Nelson.

For foods and feces we are now using a modification of a method recently described by Neumann and Meinertz.[2] In adapting this method to foods and feces we doubled the initial amount of sodium peroxide, owing to the larger sample used. It was found that moist foods, *e. g.*, meats and eggs, burned without difficulty, whereas dried foods and feces gave a good deal of trouble by frequent flashing. Since the most marked difference in these two classes of material is in their water content, we found that the addition of a small amount of water to the dried charges caused the combustion to proceed smoothly. Experience showed that the use of sodium carbonate alone, instead of a mixture of sodium and potassium carbonate, is more satisfactory, because the fusion with the former is more rapidly dissolved from the crucible by hot water, although as far as accuracy of results is concerned, we noticed no difference whether using sodium carbonate, potassium carbonate,

[1] This Journal, **26**, 1108.

[2] *Z. physiol. Chem.*, **43**, 37.

or a mixture of the two. One charge is used for the determination of both sulphur and phosphoric acid, as formerly. The method of Neumann and Meinertz, as adapted to the burning of foods and feces and now in use in the Bureau, is as follows:

Four grams of fresh foods, 2 grams of dried foods or 1.5 grams of dried feces are brought into a nickel crucible of 100 cc. capacity. The dry charges are moistened with 2 cc. of water, 5 grams of anhydrous sodium carbonate, and 5 grams of sodium peroxide are added, and the charge mixed intimately. With feces, the addition of sodium peroxide can be made all at once, but with dried foods half is stirred in and then after standing a short time, the remainder is added. This is to avoid the sudden combustion which sometimes takes place, if all the peroxide be added at once, probably due to the more highly carbonaceous character of this latter class of materials. The crucible is placed over a low, alcohol flame, and heated until the material is dry, usually requiring about half an hour; the flame is then increased, and the charge heated until it disintegrates, and can be easily broken up into a powder. The crucible is removed from the flame, the powdered charge covered with sodium peroxide and heated until liquid, starting with a moderate flame and increasing to an intense blast. When the liquid state is reached, a little peroxide is added to insure complete oxidation, the crucible allowed to cool, and the fusion dissolved out with hot water, and treated exactly as described for the Osborne method.

The advantages of this method over that of burning with sodium peroxide alone, are the following:

(1) Combustion is more satisfactory. When burning by Osborne's method, charred material was often found on dissolving the fusion, making it necessary to repeat the combustion. By employing sodium carbonate with the peroxide, as described above, such cases of incomplete combustion are rare. That results agree with Osborne's method, as formerly used by us, is seen by the following table:

Substance.	Laboratory number.	Per cent. sulphur.		Per cent. phosphoric acid.	
		Osborne.	Modified Neumann.	Osborne.	Modified Neumann.
Dried feces	12154	0.707	0.715	4.32	4.32
" "	12159	0.506	0.517	5.68	5.60
" "	12161	0.612	0.606	5.72	5.68
" "	12164	0.546	0.527	5.48	5.40
" "	12170	0.561	0.546	6.44	6.52
" "	12172	0.621	0.608	4.04	4.08
" "	12173	0.561	0.569	5.92	5.88
" "	12176	0.563	0.575	5.24	5.20
" "	12178	0.583	0.586	4.32	4.28
" "	12183	0.531	0.546	5.16	5.08
" "	12184	0.610	0.611	4.24	4.28

Foods.

		Per cent. sulphur.			
Pork chops.....	.....	0.285	0.311	....	....
Veal.....	.....	0.308	0.310	....	....
Beef steak.....	.....	0.303	0.294	....	....
Chicken.....	.....	0.321	0.313	....	....
Ice cream.....	.....	0.031	0.029	....	....
Oysters (fried)...	.....	0.206	0.200	....	....
Fish.....	.....	0.264	0.261	....	....
Eggs.....	.....	0.211	0.204	....	....
—Bread.....	.....	0.163	0.183	....	....
—Potato.....	.....	0.142	0.146	....	....
—Custard.....	.....	0.183	0.186	....	....

(2) Less time and attention are required. The sodium peroxide method demands close attention, owing to the constant danger of frothing and flashing, and is consequently, extremely tedious. Furthermore, the actual combustion is slower. With the sodium carbonate modification very little attention is required, more lamps can be used, and owing to the shorter time required for combustion, many more samples can be burned in a given time.

(3) Economy of material. The amount of sodium peroxide used is usually less than in the older method.

The type of the lamp which we find most satisfactory is Barthel's alcohol burner. This lamp burns alcohol vapor, is sparing of fuel, and is capable of adjustment, ranging from a very small flame to a powerful blast.

Kiester and Theil[1] published an article recently, in which they obtained a pure barium sulphate precipitate in the presence of much iron, by adding barium chloride to the hot alkaline solution, and

[1] *Z. anorg. Chem.*, **19**, 100.

then making acid with hydrochloric acid. In this way no iron is occluded. We tried this method of precipitation with feces in order to avoid, if possible, the removal of phosphate by filtration, but the results obtained were not satisfactory.

IMPROVEMENTS IN GAS ANALYSIS APPARATUS.

By Alfred H. White and E. D. Campbell.

Received March 24, 1905.

The accuracy of gas analysis is so largely dependent on methods of manipulation and details of construction of apparatus, that it is worth while to record anything which adds to the simplicity or accuracy of existing methods. The apparatus described in this article differs only in details from the usual form of Hempel apparatus, but the changes that have been introduced have been prompted by experience, and have proven their value by actual use in our gas analysis laboratory for from four to twelve years. During this period, the glass parts of apparatus have been made from our sketches by Greiner and Friedrichs, of Ilmenau, in Thuringia, and the stands have been made in our own shops. Changes in detail have been gradually introduced in the effort to render the process simpler and more accurate, and the apparatus less liable to breakage. These sketches of our present apparatus are now presented in the belief that they represent slight improvements in simplicity, durability and accuracy.

The perspective view shows the apparatus as it appears in service, while some details are given in the other sketch. The burette-stand, it will be readily evident, is made from an ordinary iron stand, one of whose rings of external diameter slightly greater than the water jacket of the burette has been provided with a brass collar, thus making a cup in which the rubber stopper of the water jacket rests without binding. Another ring large enough to slip loosely over the water jacket, serves to keep the burette vertical. A segment is sawed out of the front of this ring to allow an uninterrupted view of the graduations, and it is wrapped with chamois skin until it fits as snugly as desired. By this simple arrangement the burette may be raised, lowered, or swung to one side at the convenience of the operator, and may be tipped in any position while carrying, without danger of breakage.

By reference to Fig. 1, it will be seen that the burette is a perfectly straight tube. It is closed at the bottom by a one hole rubber stopper, which need not even be wired in, unless the burette is to be filled with mercury. To clean the burette, all that is necessary is to take out the rubber stopper, and lift the burette and its jacket out of the rings when it may be turned upside down, and swabbed out as an ordinary burette.

The greatest source of manipulative error in gas analysis is apt to be in making the connection between the burette and pipette. Unless this is very skilfully done, there will be either loss or gain in the gas volume in transferring the gas. The three-way stop-cock shown in Fig. 1 has allowed a very satisfactory solution of the problem. By a quarter turn of the stop-cock from the position indicated in the figure, access to the burette is cut off, and communication opened from the capillary connecting tube through the horizontal bore of the cock to the outside air. The pipette may now be connected to the burette by the usual bent capillary, without any reference whatever to how much air there may be in the connections, and by means of the rubber tube shown attached to the second bulb of the pipette, the reagent may be blown over to the stop-cock expelling all air as it goes. When the reagent has reached the cock, by a quarter turn communication with the burette is established, and the gas is then passed over into the pipette. In drawing the gas back to the burette, the reagent is in the same way drawn up through the capillary tubes until it has just reached the stop-cock, and the gas is again all in the burette. A quarter turn of the cock again establishes communication with the air, and the reagent at once siphons back into its pipette. The pipette is disconnected, and the capillary connecting tube is washed out without removing it from the burette, by means of the wash-bottle shown, when everything is in readiness for another absorption. By this method of manipulation, it is easy to transfer the gas from burette to pipette without loss or inclusion of air. Furthermore, since the volume of the capillary is entirely immaterial, it may be chosen of larger diameter than usual, permitting more rapid work and lowering the pressure necessary to force the gas through it rapidly. It has been found advantageous to have the stop-cock left-handed, as indicated, so that the hand manipulating the stop-cock, may not interfere with a clear view of the meniscus of the liquid advancing along the capillary tube. The only change

in the pipettes (Figs. 2, 3 and 4) lies in the elimination of the deep U-bend from the capillary tube. The advantage of such a bend disappears with the manipulation indicated, and its elimination does away with the disadvantage caused by drops of reagent collecting in the bottom of the U, to be subsequently carried into the burette. Wooden stands are preferred to metal ones for mounting pipettes. Iron corrodes more rapidly, and the iron

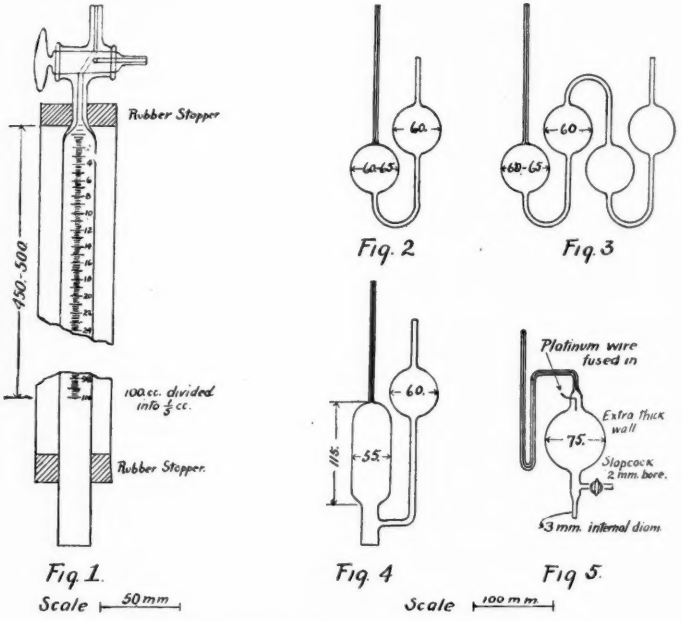


Fig. 1. Fig. 2 Fig. 3 Fig. 4 Fig. 5.

Scale 50 mm Scale 100 mm

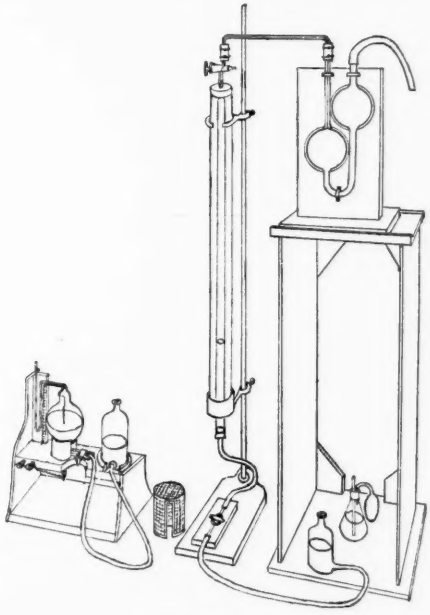
All capillary tubing to be 1 mm. internal diameter and 6-7 mm. external diameter

All dimensions in millemeters

frames are more apt to break other apparatus, if they are carelessly knocked together. The wooden stands should preferably be paraffined and not shellacked, as the shellac is more readily attacked by reagents, which may be spilled.

The explosion pipette adopts the valuable modification proposed by Gill, of introducing one of the platinum wires from the

bottom of the pipette. The difficulty of keeping the joints of the Gill pipette tight, led us to change to the form indicated in Fig. 5. The upper wire is fused through the glass, while the lower is held by a column of sealing-wax, sucked while molten, through the conical stem of the pipette almost to the outlet tube. This lower platinum wire must be stiff, and should preferably be almost a millimeter in diameter. No difficulty has been experienced in making the joints tight, and the method of sealing possesses the



advantage that the distance between the two platinum wires may at any time be changed to suit the induction coil.

The stand upon which this explosion pipette is mounted is shown in the sketch. The bulb rests in a hemispherical block, which is cut away to allow the passage of the stem and side arm, asbestos paper being used as a padding to make it rest evenly. Bits of cork keep the side arm supported, and prevent a strain being brought upon it by the weight of the mercury in the rubber

tube. Fine copper wires soldered to the platinum wires lead to binding-posts as indicated. The upper wire is brought smoothly up to the capillary, and tied there with thread in order that it may not be caught by the wire basket placed over the pipette to stop the glass in case of explosion. This basket, as shown in the sketch, is of very heavy wire of about ¼-inch mesh lined with heavy 12-mesh wire screen. One side is slit so as to sit astride the capillary of the pipette, and the rough surfaces are bound with tin so that they may not catch on the wires. The bottom of the basket is cut out enough to allow manipulation of the stop-cock of the explosion pipette, while the basket is in place. The method of connecting this pipette to the burette and of transferring the gas is the same as for the other pipettes.

CHEMICAL LABORATORY,
UNIVERSITY OF MICHIGAN.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI. NO. 65.[1]]

A METHOD FOR THE DETECTION OF THE MORE COMMON ACIDS.

BY STANLEY R. BENEDICT AND J. F. SNELL.

Received April 11, 1905.

THE following systematic scheme for the detection of the acid radicals (anions) was suggested by the reasonably successful attempts of Bailey and Cady,[2] and of Abegg and Herz,[3] to reduce the analysis for anions to a system resembling that commonly used in the detection of the cations.[4]

This method, though differing radically in its present form from that of Bailey and Cady, grew out of the use of the latter with classes in the University of Cincinnati, and provides for the detection of the same anions with the addition of the nitrite and sulphide ions.

[1] Read before the Cincinnati Section of the American Chemical Society, November 9, 1904.

[2] Bailey and Cady: "A Laboratory Manual of Qualitative Analysis," 4th ed., 1901.

[3] Abegg and Herz: *Zeit. anorg. Chem.*, **23**, 236; "Chemisches Praktikum," 1900, pp. 113-114.

[4] W. A. Noyes, in the fifth edition of his "Qualitative Analysis," 1901, describes a method based on that of Abegg and Herz, but materially modified and expanded.

The distinguishing features of the method may be summarized as follows: (1) As in the methods of Bailey and Cady, and Abegg and Herz, the majority of the anions are detected and successively removed from one portion of solution. The older and more common procedure of testing for each anion in a separate portion of the solution has the disadvantages of using more substance and of requiring a more exhaustive knowledge of possible "interferences" than can reasonably be expected of a beginner. (2) The groups are made as small as possible. Indeed, wherever practicable we have provided for the removal of the anions singly or in pairs. This renders the separation within the groups very simple, and, we believe, facilitates the analysis materially. (3) The time-consuming operations of distillation and evaporation have been avoided as far as practicable. (4) Preliminary tests for the absence of certain groups of anions (not identical with the groups of the system) are introduced with the object of shortening the subsequent analysis by the omission of the tests for the ions thus proved absent.

The solution is prepared as usual by boiling with concentrated sodium carbonate solution. The boiling must be continued long enough to expel all the ammonia present. If the solution, after boiling with sodium carbonate, is blue, due to the presence of copper, it should be treated with hydrogen sulphide.

For convenience of reference the solution thus freed from cations will be designated "Solution A."

The analysis is carried out as follows:

About half of Solution A is reserved for individual tests for the anions of Group IX. Minor portions of 2-3 cc. are used for the two preliminary tests which follow, and the remaining ("major") portion is used for the precipitation of Group I.

Preliminary Test for Halogen and Nitrite Ions.—Neutralize a small portion (2-3 cc.) of Solution A with dilute sulphuric acid, add to the liquid nearly an equal volume of concentrated sulphuric acid and a small quantity of manganese dioxide, warm and test the escaping vapors with potassium iodide starch paper. If no coloration appears, bromide, chloride, iodide, chlorate and nitrite ions are absent, and the tests for them may be omitted below.

Preliminary Test for Cyanide, Arsenite and Iodide Ions.—To 1 or 2 cc. of N/25 mercuric chloride solution add a little sodium hydroxide solution. A yellow precipitate of mercuric oxide is pro-

duced. Now add 1 or 2 cc. of Solution A. If cyanide, arsenite, or iodide ions are present the precipitate will at once dissolve, forming a complex salt. If the precipitate does not dissolve, the tests for arsenite, iodide and cyanide may be omitted below.

GROUP I.—*$Fe(CN)_6''''$, SCN', $Fe(CN)_6'''$, CN', I', Br', and Cl'.*

Acidify the main portion of Solution A with dilute nitric acid (odor of sulphur dioxide at this point indicates sulphite ion; see Group V). Add silver nitrate in slight excess, filter and reserve the filtrate for lower groups. If the preliminary test has indicated the presence of halogens, divide the precipitate, after washing, into two portions.

Treatment of Portion I for the Identification of the Ferrocyanide, Ferricyanide, Sulphocyanate and Cyanide Ions.—Digest the precipitate in the cold with a mixture of three volumes of 2N sodium chloride and one volume of 5N hydrochloric acid. By this means the ferrocyanide, ferricyanide, sulphocyanate and cyanide ions are again brought into solution. Filter off and discard the precipitate of silver chloride.

$Fe(CN)_6''''$.—To the filtrate add ferric chloride in excess. A dark blue precipitate of ferric ferrocyanide shows the presence of *ferrocyanide* ion. Filter and test the filtrate for complete precipitation with a little more ferric chloride.

SCN'.—A blood-red color in the filtrate shows the presence of *sulphocyanate* ion.

$Fe(CN)_6'''$.—To the filtrate add sulphurous acid and a little more ferric chloride and warm the test-tube. A dark blue precipitate indicates the *ferricyanide* ion. The precipitate is again ferric ferrocyanide, the ferricyanide ion having been reduced to ferrocyanide ion by the sulphurous acid.

CN'.—If the preliminary test has not proved the absence of the cyanide ion, filter off the precipitate of ferric ferrocyanide, make the filtrate alkaline with sodium hydroxide and add a portion to a suspension of mercurous oxide prepared by adding a slight excess of sodium hydroxide to N/25 mercurous nitrate solution. If *cyanide* ion is present the precipitate will partly dissolve, while that which remains undissolved will become light gray in color. (One portion of the mercurous oxide is oxidized and dissolved, the other is reduced to metallic mercury.)[1]

[1] Benedict : *Am. Chem. J.*, **32**, 481 (1904).

Treatment of Portion II for the identification of the iodide, bromide and chloride ions.—This may be omitted if the preliminary test has shown absence of halogens). Transfer this portion of the precipitate to a small beaker, add a few fragments of zinc, cover with water, add a few drops of sulphuric acid and warm until the entire precipitate has become black or brown in color, owing to the reduction of the silver salts to metallic silver. Filter and neutralize the filtrate with sodium carbonate. Filter off and discard the precipitate of zinc hydroxide and carbonate. To the filtrate add N/10 potassium iodate and proceed to A or B below.

A. If sulphocyanate ion is present. I'.—To a minor portion of the solution add sodium acetate and acidify with acetic acid. Liberation of iodine indicates the *iodide* ion. The liberated iodine may be detected either by coloration of the solution or by shaking out with carbon disulphide.

Br'.—Acidify the major portion of the solution with acetic acid and boil until colorless. Add a little more potassium iodate, and if coloration appears, boil again until colorless. Repeat until further addition of potassium iodate fails to produce coloration, but avoid more than a slight excess of potassium iodate. Having expelled all the iodine by boiling, add to the solution nearly one-half its volume of dilute nitric acid. Coloration (due to liberated iodine and bromine) shows the presence of *bromide* ion, which may be confirmed by shaking a portion of the solution with carbon disulphide.

Cl'.—Boil the main portion of the solution until colorless, add 1 or 2 cc. of potassium iodide solution and boil again until colorless. Now add an equal volume of concentrated nitric acid and two or three drops of silver nitrate solution. A white precipitate, insoluble on warming, shows the presence of the *chloride* ion.

B. If sulphocyanate ion is absent.—Acidify the solution (containing the potassium iodate) with acetic acid. Coloration shows the presence of the *iodide ion*, which may be confirmed by shaking a small portion of the solution with carbon disulphide. The main portion is freed from iodide and tested for bromide and chloride, as directed above under A.[1]

[1] Benedict and Snell: This JOURNAL, **25**, 809 (1903).

GROUP II.—ClO_3'.

(If the preliminary test for halogens has given a negative result, the test for the chlorate ion may be omitted.)

To a minor portion of the filtrate from Group I (which should contain a slight excess of silver nitrate) add a small piece of zinc and warm. A white precipitate of silver chloride shows the presence of the *chlorate* ion.

GROUP III.—AsO_3'''.

To the major portion of the filtrate from Group I add sodium chloride to remove the excess of silver. Filter and discard the precipitate. The major portion of the filtrate is reserved for Group IV, while a minor portion is used for the test for arsenite ion as follows: Make slightly alkaline with sodium carbonate, add barium chloride in excess, filter and reject the precipitate. Acidify the filtrate with concentrated hydrochloric acid and pass in hydrogen sulphide. A yellow precipitate shows the presence of the *arsenite* ion. (This test may be omitted, if arsenic was proved absent in the analysis for cations.)

Note.—The arsenate ion is completely precipitated by barium, while the solubility product of barium arsenite is so high that enough arsenite ion is left in solution to give the reaction with hydrogen sulphide.

GROUP IV.—SO_4''.

To the major portion of the solution from which the silver ions have been removed (see Group III) add more nitric acid and then a few drops of barium chloride solution. A white precipitate indicates the *sulphate* ion. If a precipitate is obtained, add a slight excess of barium chloride and filter.

GROUP V.—SO_3''.

The presence of the sulphite ion will usually have been indicated by the odor of sulphur dioxide obtained on acidification for Group I. To the filtrate from Group IV add more barium chloride and boil for two or three minutes. The nitric acid oxidizes the *sulphite* ion to sulphate ion, which is then precipitated by the barium ion. The boiling should be continued until all the sulphite present has been removed.

Note.—The arsenite ion, if present, is oxidized to arsenate by this treatment. Hence, unless the absence of the arsenite ion has

been proved, a test for arsenate ion in Group VII does not prove the presence of that ion in the original solution.

GROUP VI.—*C_2O_4'' and CrO_4''.*

Add more barium to the filtrate from Group V, neutralize with sodium carbonate and acidify with acetic acid. Allow to stand for a few minutes. A yellow precipitate indicates the *chromate* ion, a white precipitate the *oxalate* ion.

Note.—The chromate ion can not be present if the original solution was colorless of if chromium was not found in the analysis for cations.

Filter, to the filtrate add calcium chloride and concentrate the liquid to one-half its volume or less. A fine white precipitate confirms the presence of the *oxalate* ion, the solubility product of calcium oxalate being lower than that of barium oxalate. Filter again and use the filtrate for Group VII.

GROUP VII.—*AsO_4''' and PO_4'''.*

To the filtrate from Group VI add solid ammonium chloride, agitate until dissolved, make alkaline with ammonium hydroxide and add more calcium chloride. A white precipitate indicates arsenate or phosphate ion or both. Filter and reserve the filtrate for Group VIII.[1]

AsO_4'''.—(This test may be omitted if no arsenic was found in the analysis for cations.) Dissolve the precipitate in dilute hydrochloric acid, add sulphurous acid and boil to reduce the arsenate ion to arsenite, expel excess of sulphurous acid by boiling, add concentrated hydrochloric acid and thoroughly saturate with hydrogen sulphide. A yellow precipitate indicates the *arsenate* ion, unless arsenite ion has been found. If arsenite ion has been found, a special test for arsenate must be made in the solution from which the cations have been removed (see Group IX).

PO_4'''.—(This test may be omitted if it has already been made in the course of the analysis for cations.) Completely remove the arsenic by means of hydrogen sulphide, filter and boil out all excess of hydrogen sulphide. Add a little of this solution to an excess of a solution of ammonium molybdate, strongly acidified with nitric acid. Warm very gently and leave standing for five

[1] A fact overlooked by Abegg and Herz and apparently not generally known is that neither metaborate nor tartrate ions are precipitated by calcium in neutral or alkaline solution containing a considerable quantity of ammonium salt.

minutes. Formation of a yellow precipitate shows the presence of the *phospha'e* ion.

GROUP VIII.—BO_2' *and* $C_4H_4O_6''$.

Acidulate the filtrate from Group VII with dilute hydrochloric acid, concentrate by evaporation, and divide into two portions to be tested for borate and tartrate respectively.

BO_2'.—Portion I: Add an equal volume of concentrated sulphuric acid, cool, add two volumes of methyl alcohol and place in a thick-walled test-tube or specimen tube provided with a two-holed stopper carrying (1) a glass tube connected with the gas supply and reaching nearly to the bottom of the test-tube so that illuminating gas can be passed through the liquid; (2) a glass tube drawn to a jet and surrounded by a glass tube of greater diameter, constituting a miniature Bunsen burner. Pass illuminating gas through the tube and light it at the jet. A green flame shows the presence of the *borate* ion.

$C_4H_4O_6''$.—Portion II: Make just alkaline with ammonium hydroxide, add a little barium chloride and then a little sodium hydroxide. This will cause the formation of a white precipitate. Now make further additions of sodium hydroxide until either the precipitate has been dissolved or the solution diluted to five times its original volume. If the precipitate dissolves and is reprecipitated upon heating, the *tartrate* ion is present.

Note.—On the addition of the first portion of sodium hydroxide a precipitate is always obtained, whether the tartrate ion is present or not. In case the tartrate ion is absent this precipitate consists of barium hydroxide and carbonate, the latter due to impurity in the sodium hydroxide. These precipitates will not dissolve in excess of sodium hydroxide. If the tartrate ion is present, the precipitate consists of barium tartrate only, which readily goes into solution in an excess of the hydroxide.

GROUP IX.—S'', NO_2', NO_3', $C_2H_3O_2'$, SiO_3'' (AsO_4''').

The tests for the anions of this group are made upon minor portions of "Solution A."

S'' *and* NO_2'.—Acidify a portion with acetic acid and warm slightly. Note the odor and test the escaping gases with lead acetate paper and with potassium iodide starch paper. The test for the nitrite ion may be confirmed by acidifying another portion

of Solution A with acetic acid and adding ferrous sulphate. A brown coloration shows the presence of *nitrite* ion.

Note.—If, in removing the cations, copper was precipitated from the sodium carbonate solution by means of hydrogen sulphide, the sulphide ion will evidently be found at this point, but can not have been present in the original solution since it contained the cupric ion.

NO_3'.—Acidify a portion of Solution A with dilute sulphuric acid. In the absence of the nitrite, chlorate, iodide, bromide, chloride, ferrocyanide, ferricyanide and sulphocyanate ions, the "brown ring" test may be made upon this acidified solution as follows: Add an equal volume of concentrated sulphuric acid, cool and pour in gently a solution of ferrous sulphate, so that the two liquids do not mix. A brown ring shows the *nitrate* ion. If the nitrite ion is present, the acidified solution should be boiled until the nitrous acid is completely expelled. It may then be used for the "brown ring" test. The other ions above enumerated as interfering with this test may be removed by treatment of the solution with zinc and boiling (necessary only if chlorate ion be present) followed by the addition of silver sulphate in slight excess. Filter and use the filtrate for the test.

The following well-known test may also be used in the absence of, or after the elimination, as above, of the nitrate and chlorate ions. Add a few drops of the solution to a mixture of equal parts of phenol and concentrated hydrochloric acid and heat to boiling. Add a decided excess of sodium hydroxide. An intense green color, becoming dark blue on dilution of the solution, shows the presence of the nitrate ion.

$C_2H_3O_2'$.—Acidulate a portion of Solution A with dilute sulphuric acid, boil to expel oxides of nitrogen, if present, then make slightly alkaline with sodium carbonate. Add silver nitrate in slight excess to remove anions of other weak acids and filter. Add sodium chloride to remove excess of silver ions and filter. Saturate the filtrate with hydrogen sulphide. In another test-tube acidulate 2 to 3 cc. cobalt nitrate solution with two or three drops of normal acetic acid solution and saturate with hydrogen sulphide (the slight quantity of black precipitate formed may be filtered off or disregarded). Now add a portion of the test solution (prepared as above) to the cobalt solution. An *immediate heavy* pre-

cipitate of cobaltous sulphide proves the presence of the *acetate* ion.[1]

In the absence of the cyanide, chromate, chlorate and iodide ions the well-known test for acetate with concentrated sulphuric acid and alcohol (formation of ethyl acetate) may also be used.

SiO_3''.—Acidify a portion of the solution with hydrochloric acid, evaporate to dryness, gently heat the residue, then treat with dilute hydrochloric acid and afterwards with hot water. An insoluble residue indicates the *silicate* ion. Confirm by the usual bead tests, *viz.*, skeleton in metaphosphate, transparency in sodium carbonate bead, or by treatment with hydrofluoric acid.

$As.O_4'''$.—(To be used in case the arsenite ion has been found.) If arsenite ion has been found in Group III, the appearance of arsenate ion in Group VII does not prove the presence of that ion in the original solution (see note on Group V). To test for the arsenate ion in such an instance, to a portion of Solution A add magnesia mixture as long as a precipitate forms, filter out and wash the precipitate, dissolve it in concentrated hydrochloric acid, add a little sulphurous acid and boil until the excess is completely expelled. Pass in hydrogen sulphide. A yellow precipitate of arsenious sulphide indicates the arsenate ion.

GROUP X.—CO_3''.

Acidify the original solution or substance with dilute hydrochloric acid and test the escaping gas with a film of lime-water.

SOME NEW FORMS OF LECTURE AND LABORATORY APPARATUS.

BY G. B. FRANKFORTER AND FRANCIS C. FRARY.

Received April 10, 1905.

THE following pieces of apparatus will, we believe, be of some little interest to those who are teachers of chemistry. These forms of apparatus have been used both on the lecture table and in the laboratory, and have given such satisfactory results that we venture to give them a brief notice.

One of the essentials in both lecture and laboratory apparatus is simplicity in construction and manipulation. If a piece of apparatus will give good results in the hands of the average student,

[1] Benedict: *Am. Chem. J.*, **32**, 481 (1904).

it may be considered as having some merit. If it does not, it will certainly have a short life. The apparatus described below has given good results in this laboratory, and we hope that it may prove useful to others.

Apparatus for the Determination of the Hydrogen Equivalent of Zinc.—Various pieces of apparatus have been used on the lecture table and in the laboratory for determining the hydrogen equivalent of zinc, but none which we have tried proved free from faults, especially in the hands of the students. The apparatus described below, will, we believe, eliminate the chief sources of error in this determination.

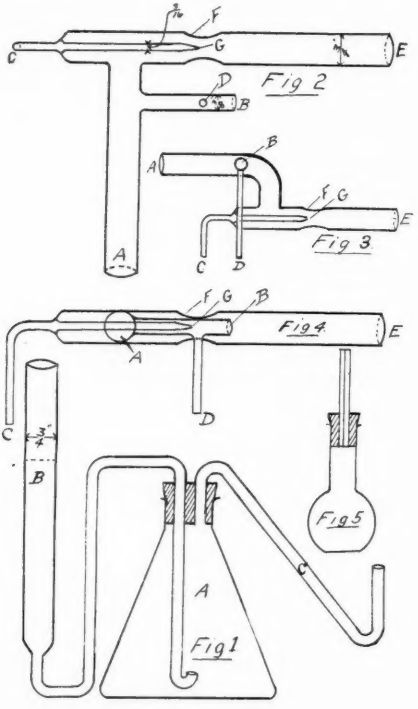
As shown in Fig. 1, it consists of an Erlenmeyer flask A of about 200 cc., fitted with a double-bored cork. Through one hole passes a funnel tube bent in the form of an S, and with the funnel part extended into a wide tube. The shape of the funnel tube is the only peculiar part of the apparatus. By using a wide tube, so that the liquid always stands in the wide part, acid may be introduced without any danger of carrying air bubbles into the flask. The zinc is placed in the flask, the whole apparatus is filled with freshly boiled water, and sulphuric acid (100 cc. of acid 1 : 4) is poured into the funnel tube. The hydrogen liberated is collected in a measuring tube over water. The last trace of gas is driven out of the apparatus by pouring water into the funnel tube. Calculations are made in the usual manner.

APPARATUS FOR MAKING SULPHURIC ACID.

The old apparatus, described in nearly all the large text-books, must be admitted by every one to be unsatisfactory for laboratory use. For instance, it is not satisfactory to make sulphur dioxide from sulphuric acid and copper, for the student will immediately see that you are making sulphuric acid from sulphuric acid, instead of sulphur or pyrites. The apparatus described below, we believe to be an improvement upon the old form both in construction and manipulation.

The apparatus, Figs. 2 and 4, is clamped in such a position that tubes A and E are almost horizontal, A being slightly higher than E. Tube C is connected with a flask of boiling water, provided with a safety tube, for supplying steam under pressure, and tube D with a nitric oxide generator. E is connected with a Liebig condenser by means of a short piece of rubber tubing. The other

end of the condenser projects into a large bottle or flask. As soon as steam and nitric oxide are passing through the apparatus, a porcelain boat full of burning sulphur is introduced into A, and the process begins. Enough acid for experimental purposes may be made in a few minutes. The apparatus can be made by any one with a moderate knowledge of glass-blowing, and when made



of good glass there is little danger of breakage. Fig. 3 represents the apparatus used for lecture work. The apparatus is best used under a hood, but may be used on any table by placing a beaker containing a little ammonia near the neck of the large bottle or flask, so as to absorb the oxides which escape.

CHARLES' LAW.

The apparatus used in proving Charles' Law consists of a small,

flat-bottomed flask of about 100 cc. The flask is fitted with a single-bored cork, through which passes a fine, capillary tube about 4 inches long. The cork is pressed into the neck of the flask as far as it will go, and the capacity of the flask determined. The position of the cork is marked by a scratch on the neck of the flask.

The flask is thoroughly dried, and the cork containing the capillary tube is pressed into the neck until the lower end is even with the scratch. Using the capillary tube as a handle, the flask is immersed in a bath of boiling water. It is held in this position until the air in the flask has reached the temperature of the water. The temperature is then taken. The finger is moistened and placed over the end of the capillary tube, the apparatus is transferred to a bath of cold water, capillary end first, and the finger removed. As the apparatus cools, the water enters the flask, the quantity of water measuring the change in the volume of the air. From the data thus obtained, the law may be verified.

Care must be taken to handle the apparatus by means of the capillary tube so as to avoid the error due to the heat of the hand. The chief cause of error is that due to imperfect drying of the apparatus, especially the cork, capillary and the space between them.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

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THE SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE SOLUTIONS.

BY ARTHUR A. NOYES AND WILLIAM H. WHITCOMB.

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I. HYPOTHESES AS TO THE CAUSE OF THE SOLUBILITY-INCREASE.

IT IS A well-known fact, and one often made use of in chemical analysis, that lead sulphate, though difficultly soluble in water, dissolves in considerable quantity in a strong ammonium acetate solution. As to the magnitude of this solubility we have, however, been able to find only two quantitative statements, that of Long,[1] and that of Bischof,[2] both of which relate to very concentrated solutions of ammonium acetate.

[1] *Am. Chem. J.*, **22**, 217 (1899).
[2] Comey's "Dictionary of Solubilities."

There has, moreover, been offered no verified explanation of the large increase in solubility which ammonium acetate produces. It seems, however, probable that the effect arises from one of the three following causes, or from a combination of them: (1) lead acetate is a slightly ionized substance, and therefore, a large quantity of it is produced in the solution by metathesis; (2) intermediate cathions containing lead in combination with the acetate ion $PbC_2H_3O_2^-$ are formed; (3) complex cathions of the composition $Pb(NH_3)_x^{++}$ are produced by combination of the lead ion with the free ammonia resulting from the hydrolysis of the salt.

These three hypotheses can be tested by migration experiments, for, in the first case, the lead, being present only as an un-ionized compound, would not move at all, while in the second or third case, it would migrate with the positive current. The first and second hypotheses can further be tested by determining the degree of ionization of lead acetate and its change with the dilution by conductivity measurements or otherwise. Furthermore, both the first and second hypotheses evidently require that sodium acetate (or any other di-ionic acetate) have nearly the same effect on the solubility of lead sulphate as ammonium acetate, while, on the other hand, the third hypothesis would lead to the expectation that the sodium salt would have a much slighter effect. The third hypothesis may seem to be inconsistent with the fact that lead hydroxide is but little soluble in ammonium hydroxide, but it is not necessarily so, since in the latter solvent the hydroxyl-ion concentration may be large enough to keep down the concentration of the lead ion and therefore that of the complex ion, if this were not very stable. This hypothesis would, however, evidently require that neutral ammonium acetate, owing to its greater hydrolysis, be a much better solvent for lead sulphate than neutral ammonium nitrate or chloride; that these different salts behave nearly alike if a moderate proportion of ammonium hydroxide be added to their solutions; and that the addition of acetic acid greatly reduce the solvent power of ammonium acetate. These last requirements seem, indeed, to be at variance with analytical experience.

II. PREVIOUS MEASUREMENTS RELATING TO THE SUBJECT.

There already exists some evidence that lead acetate is much

less ionized than other salts of the same type, and, therefore, that the first hypothesis furnishes the true explanation of the increase in the solubility of lead sulphate. Thus, the freezing-point measurements of Kahlenberg[1] indicate an ionization of only 19 per cent. in $\frac{1}{4}$ molal, and of 37 per cent. in $\frac{1}{8}$ molal solution. Moreover, an isolated measurement of the conductance of the salt in 1-40 molal (1-20 normal) solution at 25° by Trey,[2] gave a value corresponding to an equivalent conductivity of 32.0 in reciprocal ohms or to a degree of ionization of 28.4 per cent.; and a series by Ley[3] beginning with 1-32 normal gave at this concentration an equivalent conductivity of 37.6 reciprocal ohms corresponding to an ionization of 33.4 per cent. Evidence against the third hypothesis is furnished also by the results of Dibbitts,[4] who found that sodium acetate also increases greatly the solubility of lead sulphate; he found namely, that 100 cc. of a solution containing 2.05 grams sodium acetate dissolves 0.054 gram lead sulphate, and 100 cc. of one containing 8.20 grams sodium acetate dissolves 0.900 gram lead sulphate.

The subject seemed, however, to deserve fuller investigation, and we have, therefore, done some further work upon it. This has consisted in qualitative migration experiments with solutions of lead sulphate in ammonium acetate, measurements of the conductivity of aqueous solutions of pure lead acetate, accurate determinations of the solubility of lead sulphate in ammonium acetate solutions, and a single rough one in a sodium acetate solution. It is the purpose of this article to present the results, and discuss their significance.

III. CONDUCTIVITY OF LEAD ACETATE SOLUTIONS.

The sample of lead acetate used in our experiments was prepared by crystallizing the chemically pure commercial salt four times from hot water containing acetic acid, and once from pure water. It was dissolved in conductivity water, and the solution was standardized by precipitation with sulphuric acid and weighing the lead sulphate. Two solutions were so prepared at different times. The first contained 1.420 equivalents (0.710 mol) per

[1] *Z. phys. Chem.*, **17**, 583 (1895).
[2] *Ibid.*, **22**, 433 (1897).
[3] *Ibid.*, **30**, 246 (1899).
[4] *Dingler polytech. J.*, **210**, 475; *Z. anal. Chem.*, **13**, 137.

liter. The second contained 0.5088 equivalent (0.2544 mol) per liter.

The measurements were made at 25° by the Kohlrausch method, using a resistance vessel of the Arrhenius type, the resistance capacity or cell-constant of which was determined by measurements with 0.01 normal potassium chloride solution. The results are all expressed in reciprocal ohms. The value of the equivalent conductivity (Λ_0) at infinite dilution (112.8) used in calculating the conductivity ratio (Λ/Λ_0), which corresponds to the degree of ionization, if the salt dissociates only into Pb^{++} and Ac^{-} ions, was calculated from the values for the individual ions at 18° given by Kohlrausch and Grüneisen[1] ($\Lambda_{Pb}=61.1$ at 18°), and by Kohlrausch and Steinwehr[2] ($\Lambda_{Ac}=35.0$ at 18°), and from the temperature-coefficients computed by Kohlrausch.[3]

The first solution above referred to was diluted four times in succession with conductivity water by means of two graduated flasks in such a way that the concentration was each time reduced to one-fourth of its former value. The value of the cell-constant (or the factor by which the actual conductance must be multiplied to give the specific conductance) in this series of experiments was 0.1389.

A second series of measurements was carried out with greater care with the second solution, it being diluted in a somewhat different manner from the first. The stock solution was kept in a Jena flask, from which it was drawn as required, air being admitted through a soda-lime tube. Twofold dilutions were made by weighing, the volume concentrations being calculated with the help of a specific gravity determination. The value of the cell-constant was 0.1400 in the case of the first two measurements of the series, 0.1243 in the other cases.

The results of the measurements are given in Table I.

TABLE I.—CONDUCTIVITY OF LEAD ACETATE AT 25°.

Equivalents per liter.	Actual conductance.	Equivalent conductivity.	Conductivity ratio × 100.
	First Series.		
0.3550	0.03457	13.50	12.0
0.0888	0.01627	25.38	22.5
0.0222	0.007035	43.74	38.8
0.00555	0.002790	68.75	60.9

[1] *Berliner Sitzungsber. d. Akad. d. Wissenschaften*, 1904, p. 1221.
[2] *Ibid.*, 1902, p. 587.
[3] *Ibid.*, 1901, p. 1026; *Z. phys. Chem.*, **43**, 511.

Equivalents per liter.	Actual conductance.	Equivalent conductivity.	Conductivity ratio × 100.
	Second Series.		
0.5088	0.04220	11.61	....
.....	0.04209	11.58	....
.....	0.04762	11.63	....
.....	0.04772	11.66	....
.....	0.04735	11.57	....
.....	0.04770	11.65	....
.....	Mean	11.62	10.3
0.2544	0.03345	16.34	....
.....	0.03346	16.34	....
.....	0.03345	16.34	....
.....	0.03368	16.45	....
.....	0.03361	16.42	....
.....	0.03365	16.43	....
.....	Mean	16.39	14.5
0.1272	0.02272	22.19	....
.....	0.02274	22.21	....
.....	0.02271	22.18	....
.....	Mean	22.19	19.7

The mean values of the equivalent conductivity derived from these two independent series of experiments (after being corrected with help of the formula referred to just below, to a round dilution not differing much from that at which the measurements were made) and the above-mentioned results of Trey and of Ley (expressed in reciprocal ohms instead of in mercury-units as given by those authors) are for the purpose of better comparison, summarized in Table II. The table also contains the corresponding value of the conductivity-ratio ($\Lambda/\Lambda_0 = \gamma$) multiplied by 100, and the values of the empirical function $100\,(\gamma\,C)^2/C(1-\gamma)$ where C is the equivalent concentration, which function was found to be fairly constant when applied to our own data between ½ and $^1/_{12}$-normal.

TABLE II.—SUMMARY OF EQUIVALENT CONDUCTIVITY VALUES.

Liters per equivalent.	Investigator.	Equivalent conductivity.	Conductivity ratio × 100.	$\frac{100(\gamma)C^2}{(1-\gamma)C}$
2	N. & W., 2nd Ser.	11.73	10.4	0.6019
3	N. & W., 1st Ser.	13.99	12.4	0.5808
4	N. & W., 2nd Ser.	16.47	14.6	0.6256
8	N. & W., 2nd Ser.	22.45	19.9	0.6148
12	N. & W., 1st Ser.	26.05	23.1	0.5800
20	Trey	32.00	28.4	0.5635
32	Ley	37.63	33.4	0.5234
48	N. & W., 1st Ser.	44.89	39.8	0.5461

Liters per equivalent.	Investigator.	Equivalent conductivity.	Conductivity ratio × 100.	$\frac{100(\gamma C)^2}{(1-\gamma)C}$.
64	Ley	46.98	41.7	0.4662
128	Ley	57.40	50.9	0.4121
192	N. & W., 1st Ser.	69.94	62.0	0.5264
256	Ley	68.23	60.5	0.3623
512	Ley	79.09	70.1	0.3209
1024	Ley	89.29	79.2	0.2947

It will be seen from the last column that the conductivity value of Trey corresponds well with ours, but that those of Ley are considerably less, especially in the dilute solutions (1/128 to 1/256 normal).

The results show clearly that lead acetate is much less ionized than is usual with unibivalent salts, which are commonly 70-75 per cent. ionized in 0.1 normal solution. The results of Ley with other acetates of this type show too that even these have a much higher conductivity than lead acetate; thus for 1/32-normal solutions he obtained the following equivalent conductivities in reciprocal ohms: barium acetate, 80.0; manganese acetate, 66.6; nickel acetate, 64.6; cobalt acetate, 65.9; zinc acetate, 62.3; and cadmium acetate, 54.5; while that of lead acetate is only 37.6.

The actual values of the conductivity-ratio given in the table are not to be regarded, however, as a true measure of the ionization, for it is very probable in view of its slight degree of ionization that this salt forms the intermediate ion $PbAc^+$ in large quantity.

Moreover, since the Λ_0 value for dissociation into the two ions $PbAc^+$ and Ac^- would be very different from that for dissociation into the three ions Pb^{++} and $2Ac^-$, which last was assumed in computing the ratio, it is not proved by the constancy (in the stronger solution) of the function given in the last column that the former kind of ionization alone takes place, but only that the latter kind is not the exclusive one.

IV. MIGRATION EXPERIMENTS.

Two series of qualitative migration experiments were made. In one of these, the solutions, in order to avoid stirring, were gelatinized by the addition of agar; in the other, to eliminate the possibility of any influence of the agar upon the lead salt, difference in specific gravity was alone relied upon.

In the former series a U-tube 1.75 cm. in diameter and 15 cm. in height was used. The bend was filled with an agar jelly made

up with a normal ammonium acetate solution and containing zinc sulphide in suspension. Above this in each arm of the tube were placed, first, a plug of jelly 0.5 cm. long with ammonium acetate solution alone; next, one also saturated with lead sulphate; then, another one 0.5 cm. long with ammonium acetate alone; then, one with this salt in solution and zinc sulphide in suspension; and finally, some ammonium acetate solution without agar, in which platinum-wire electrodes were placed. The tube was immersed in a bath of ice water. The electrodes were kept at a potential difference of 80 volts for two hours, but at no point did the zinc sulphide become blackened, showing that the lead did not migrate to an appreciable extent in either direction.

Of the experiments made with solutions without agar added, only the final and most conclusive one need be described. The apparatus used consisted essentially of two U-tubes connected by side-arms, one of the tubes being joined at the bottom of the bend to a glass tube of small bore. The tubes were completely filled with half-normal ammonium acetate solution; then both arms of one of them were tightly stoppered, and by means of suction applied to both arms of the other, a normal solution of ammonium acetate saturated with lead sulphate and strongly colored with rosaniline hydrochloride was slowly drawn up through the small glass tube at the bottom until the bend was sealed. The solutions had been brought to a constant temperature of 25° previous to the filling, which took place immediately over the thermostat. A difference of potential of 110 volts was applied and the current (of 0.2 ampere) was passed for two hours. The length of the column of solution was 73 cm., thus giving a drop in potential of 1.5 volts per centimeter. The color boundary remained sharp, and nearly stationary, showing there was no stirring. At the end of the experiment, successive portions were carefully withdrawn by means of a pipette from both arms of the tube containing the dissolved lead sulphate, almost down to the color boundary. To each of these portions was added potassium chromate, which furnishes a very delicate test for lead even in acetate solution. None of the portions from the cathode side gave any indication of lead, even down to the line of separation. In the portions on the anode side there was a trifling quantity of lead in the portion immediately adjoining the lead sulphate solution, but a portion 2.4 cm. away gave no precipitate whatever with the potassium chromate. An ordinary lead ion,

for example, in a 0.2 normal lead nitrate solution, moves under a potential gradient of 1 volt per centimeter about 0.00040 cm. per second, so that under the conditions of our experiment, it would have moved about $0.00040 \times 1.5 \times 7200 = 4.3$ cm., while, in fact, no considerable quantity of the lead migrated more than a small fraction of a centimeter. On the other hand, the SO_4 ions migrated several centimeters in the same time, for a precipitate of barium sulphate was obtained in all the portions from the anode arm upon the addition of barium chloride and acidifying with hydrochloric acid, while the solution in the cathode arm gave no such indication of the presence of sulphate.

Both of these series of experiments lead to the same conclusion, namely, that substantially all the lead exists in the acetate solution in the form of un-ionized compound.

V. EXPERIMENTS ON THE SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE SOLUTIONS.

Since ammonium acetate is very hygroscopic, it is impracticable to obtain a solution of known strength by weighing out the salt. The solution was, therefore, prepared by the neutralization of ammonium hydroxide with acetic acid. Pure ammonia, free from amines, was prepared by the following method:[1] Commercial ammonium chloride, "free from hydrocarbons," was dissolved in enough boiling water to form a saturated solution. One-tenth of its volume of nitric acid (sp. gr. 1.42) was added, and the solution boiled until there was no further evolution of chlorine. The solution was then allowed to cool, the crystallized salt dissolved in water, one-twentieth of its volume of nitric acid added, and the solution again boiled as long as chlorine was given off. After diluting sufficiently to form a nearly saturated solution when cold, the salt was decomposed by lime. The ammonia was absorbed in conductivity water, carbon dioxide being carefully excluded by the use of soda-lime tubes. The ammonium hydroxide solution so obtained was standardized with the help of methyl orange against a solution of pure hydrochloric acid, whose strength had been determined by precipitation with silver nitrate. An acetic acid solution was prepared by diluting glacial acetic acid with water. It was standardized with the help of phenolphthalein against a barium hydroxide solution, which had been titrated against the

[1] Bender u. Erdmann: "Praparatenkunde," p. 234.

hydrochloric acid. The standardizations were made by weight, so as to give the number of grams of acetic acid solution which were equivalent to 1 gram of ammonium hydroxide solution. The neutral ammonium acetate solution was then prepared by adding to a given weight of the latter solution the appropriate weight of the former. Taking into account also the specific gravity of the two solutions, the concentration of the ammonium acetate solution so obtained was calculated to be 0.4141 equivalent per liter. The lead sulphate used was prepared by precipitating the commercial chemically pure lead acetate from solution by sulphuric acid, dissolving the precipitate in pure ammonium acetate, and reprecipitating with sulphuric acid.

For the determination of the lead dissolved in the ammonium acetate solution, two methods were tested by using known weights of pure lead sulphate. The first consisted in precipitation as lead chromate from acetic acid solution, filtering upon a Gooch crucible and drying at 170°; the second in precipitation as lead sulphate by sulphuric acid, filtering upon a Gooch crucible, washing first with dilute sulphuric acid and then with 50 per cent. alcohol, and drying at 170°.

The former method gave results about 0.7 per cent. too high, owing probably to the carrying-down of an excess of chromic acid; the latter method gave results which trial analyses showed to be accurate within 0.05 per cent.

The solutions were saturated by rotating the ammonium acetate solutions with a large excess of solid lead sulphate for fifteen hours within a thermostat at 25° in the manner previously described[1]. In half the determinations (marked *s* in the table below) the equilibrium was approached from the supersaturated side, by cooling a solution which had been shaken with the salt at a higher temperature, while in the other half (marked *u* in the table) it was approached from the undersaturated side, by heating the solution from the room temperature to 25°. It will be seen that the two procedures gave substantially identical results.

Table III contains the results obtained, the solubility of the lead sulphate as well as the concentration of the ammonium acetate being expressed in the first three columns in millimols per liter. In the fourth column the solubility in grams per liter is added. For comparison, is included also the solubility in pure

[1] Noyes: *Z. phys. Chem.*, **9**, 606 (1892).

water, or rather the concentration of the ionized portion in the saturated solution in water, as determined by Böttger[1] by conductivity measurements.

TABLE III.—SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE SOLUTIONS AT 25°.

Concentration of $NH_4C_2H_3O_2$.	Solubility of $PbSO_4$. Separate determ.	Mean millimols per liter.	Mean gms. per liter.
0.0	.....	0.134	0.041
103.5	2.10 *s*	2.10	0.636
.....	2.10 *u*		
207.1	4.54 *s*	4.55	1.38
.....	4.56 *u*		
414.1	10.12 *s*	10.10	3.06
.....	10.09 *u*		

It is seen from the table that the solubility is about fifteen times as great in 0.1 normal ammonium acetate solution as in water and that it increases with increasing concentration of the salt somewhat, but not very much, more rapidly than proportionality between solubility and concentration would require.

It seems certain from the conductivity and migration experiments above described that this increase of the solubility is mainly due to the formation of un-ionized lead acetate, accompanied, of course, by the production of an equivalent quantity of ammonium sulphate, which would exist partly as ions and partly as un-ionized molecules. Assuming now that the solubility product, $C_{Pb} \times C_{SO_4}$, retains the same value as in pure water, the solubility in any ammonium acetate solution might be computed if it were possible to determine the resulting concentration of un-ionized lead acetate,—a quantity which is substantially equivalent to that solubility. Unfortunately, however, our knowledge of the ionization-relations, not only of lead acetate itself, but also in general of mixtures of salts which do not conform to the mass-action law is still very imperfect, and any assumption that may be made, especially with regard to the slightly ionized lead acetate, is arbitrary. Nevertheless, it is perhaps not without interest to determine whether the solubility-change with the concentration is satisfactorily explained if it be assumed that this salt follows the mass action law (which may well be true in virtue of its small ionization tendency) and that ammonium sulphate follows

[1] *Z. phys. Chem.*, **46**, 604 (1903).

the empirical law which has been shown to apply to mixtures of largely ionized salts[1]. We then have the equilibrium equations:

$$C_{Pb} \times C_{SO_4} = S_o^2; \; C_{Pb} \times C^2_{Ac} = K_1 C_{PbAc_2}; \text{ and } C_{Am} \times C_{SO_4} = K_2 C_{Am_2SO_4} C_i^m,$$

where S_o is the solubility of lead sulphate in pure water, K_1 and K_2 are equilibrium-constants, m is an empirical exponent, and C_i is the total concentration of all the positive or negative ions in the solution. Furthermore, if S is the solubility of lead sulphate in a solution of ammonium acetate of concentration C and ionization γ, the following relations given by the conditions of the problem also hold true approximately:

$$C_{PbAc_2} = S; \; C_{SO_4} + C_{Am_2SO_4} = S; \text{ and } C_{Am} = C_{Ac} = C_i = C\gamma.$$

Combining these equations we get:

$$S = \frac{S_o}{\sqrt{K_1}} (C\gamma) \left(1 + \frac{1}{K_2} (C\gamma)^{1-m} \right)^{\frac{1}{2}}$$

Now Kohlrausch's conductivity measurements at 18° with potassium sulphate, whose ionization relations may be assumed identical with those of ammonium sulphate, show that $m = 0.59$ and $K_2 = 0.881$ when computed for the concentrations between 0.1 and 0.5 normal. The preceding equation therefore becomes

$$S = \frac{S_o}{\sqrt{K}} C\gamma \left(1 + 1.135 (C\gamma)^{0.41} \right)^{\frac{1}{2}}.$$

It will be seen at once that this equation requires that the solubility increase a little more rapidly than the ionic concentration of the salt. By means of it the solubility at the two concentrations, 0.1036 and 0.414 molal can be computed from that in the 0.207 molal solution, the value of $S_o/\sqrt{K_1}$ being first calculated from the data for the latter. For these purposes we have obtained γ from the conductivity data of Kohlrausch at 18° for sodium acetate, whose ionization relations doubtless correspond closely to those for ammonium acetate. We have thus calculated the solubility at the other two concentrations and found it to be that shown in the following table. The concentrations of the ammonium acetate are here expressed in equivalents and those of the lead sulphate in millimols per liter.

[1] See Noyes: *Science*, **20**, 577 (1904); *Tech. Quart.*, **17**, 293 (1904); This JOURNAL, **27**, R. 203.

TABLE IV.—OBSERVED AND CALCULATED SOLUBILITIES OF LEAD SULPHATE.

Concentration of $NH_4C_2H_3O_2$.	Ionization of $NH_4C_2H_3O_2$.	Solubility of $PbSO_4$.	
		Observed.	Calculated.
0.1035	0.775	2.10	2.34
0.2071	0.724	4.55	....
0.4141	0.652	10.10	8.56

It will be seen that the change of solubility with the concentration is roughly, and only roughly, that required by the foregoing formula.

Finally it may be mentioned that, to determine whether the requirement of the hypothesis is fulfilled that sodium acetate has nearly the same effect on the solubility of lead sulphate as ammonium acetate, normal solutions of these two substances were shaken occasionally at room temperature for two days with an excess of solid lead sulphate, and a 100-cc. portion of each was analyzed for its lead-content. The ammonium acetate solution yielded 0.42 gram and the sodium acetate solution 0.45 gram of lead sulphate. These experiments were very rough ones, for the solutions were made up by weighing out the commercial "chemically pure" salts without thorough drying, the temperature was variable, and complete saturation may not have been reached. Still they certainly show that the two salts have, at least roughly, the same effect.

VI. SUMMARY.

New measurements of the conductivity of lead acetate solutions at 25° between 1/2- and 1/192-normal, have been presented, which show that this salt has an abnormally small degree of ionization (only about 22 per cent. at 0.1 normal, assuming that it dissociates directly into three ions).

Qualitative migration experiments made with a saturated solution of lead sulphate in normal ammonium acetate solution have been described, which show that the lead in this solution is not present to an appreciable extent in the form of either a positive or negative ion.

The solubility of lead sulphate (in millimols per liter) has been found to be 2.1 in 0.104 normal ammonium acetate solution, 4.55 in 0.207 normal, and 10.1 in 0.414 normal. The solubility is very much greater than that in pure water (0.134 millimol per liter according to Böttger), and is roughly proportional to the concen-

tration of the ammonium acetate. Rough comparative experiments with sodium acetate and ammonium acetate showed that the solubility of lead sulphate in solutions of these two salts is of about the same magnitude.

These facts all indicate that the increased solubility of lead sulphate in acetate solutions arises mainly from the formation of unionized lead acetate by metathesis.

April, 1905.

NOTE.

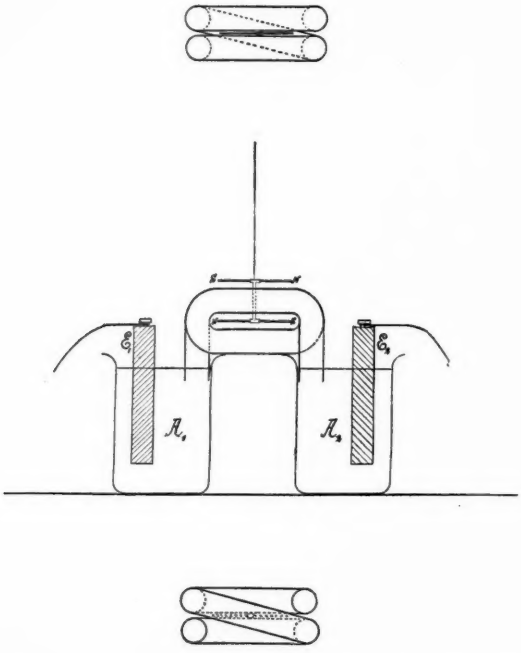
A Method of Measuring Electric Currents in Solutions for Lecture Purposes.—In order to demonstrate the existence of electric currents in electrolytes it has always been necessary to use measuring instruments in an external metallic circuit. Such methods furnish but indirect information about the direction and intensity of the current in the solution.

The instrument described below, remedies these deficiencies. It permits the direct measurement of the currents passing through the interior of a cell, and renders it possible to demonstrate the analogy of electrolytic and metallic conduction by a simple and comprehensive lecture experiment.

The apparatus consists of two half-cells A_1 and A_2 which contain exchangeable electrodes E_1 and E_2 immersed in the electrolytes that are to be examined. A glass tube, having the shape of a solenoid with one or two coils, and filled with a well-conducting solution, furnishes the electrolytic connection between the cells; while the external current can be closed by means of a switch connected by wire with both electrodes. With the aid of this arrangement it is possible to construct any galvanic cell. If, for instance, EE_1 is a carbon plate in nitric acid, E_2 a zinc electrode in dilute sulphuric acid, the common Bunsen element is formed, the solenoid playing the rôle of a porous cell. If E_1 is lead, E_2 lead covered with peroxide, and the liquid throughout the cell sulphuric acid, a storage cell is obtained, etc. As soon as the external circuit is established, discharge of the ions takes place at the electrodes, and there is a continuous migration through the electrolyte in the solenoid. That the internal current thus formed is actually identical with the current in the metallic circuit (but of opposite direction, from the negative to the positive plate when used as a

battery) is shown by the deflection given an astatic needle, which swings freely in the coils of the solenoid over a graduated scale.

The deviation, which amounts to nearly 90°, if a difference in potential of over 1 volt exists between E_1 and E_2 (as is the case



in most of the common cell combinations), and if the solenoid is filled with concentrated solutions, can be made visible in the lecture room by aid of a mirror attachment. For exact observations, or for measuring feeble currents, such as are formed if identical electrodes in solutions of slightly different concentration are used, the instrument should be put under a glass case, or readings made with the telescope.

The following dimensions were used in the construction of the electrolyte galvanometer:

Half-cells—Jena beakers of about 100 cc.

Solenoid—Thickness of walls, 0.7 mm.; inner diameter of tube,

8 to 12 mm.; total length of tubing, 25 cm.; inner long axis of solenoid, 4 cm.; inner short axis, 0.5 cm.; length of needles, 2 to 3 cm.; distance of the two needles, 15 mm.; surface of electrodes, about 100 sq. cm.

The whole is mounted on a stand of the kind used in electroanalysis. The electrodes are fixed in electrode holders, and the astatic needle is suspended by a cocoon fiber to the glass rod, which for this purpose is bent at the top. The external circuit should pass at a distance of at least 10 cm. from the solenoid, in order to avoid any disturbing influence upon the needle.

Using polished platinum plates as electrodes and 30 per cent. sulphuric acid as an electrolyte, the instrument showed a total internal resistance of about 50 ohms. The resistance did not change more than 0.5 per cent. when electrodes of somewhat different size were used, or when they were moved as much as 2 cm. from their original position, nor did filling of the fluid in the cells to different levels cause an appreciable change in the resistance. The total resistance of the instrument is always very nearly equal to the calculated resistance of the solenoid. These facts simplify the calculation of results, if the instrument is used for measuring purposes.

It may be mentioned that the electrolyte galvanometer can be used to advantage for measuring alternating currents. For this purpose it is only necessary to fill it with sodium phosphate solution, and to use one aluminium and one platinum electrode. Owing to the insulating layer of aluminium oxide, which is formed instantaneously if aluminium acts as anode, the current (as Graetz and others have shown) can only pass in one direction, and the direct current thus formed deflects the needle. A rational scale may be easily graduated by comparison with an electrodynamometer.

OSCAR ECKSTEIN.

KENT CHEMICAL LABORATORY,
UNIVERSITY OF CHICAGO.

REVIEW OF FOREIGN WORK IN AGRICULTURAL CHEMISTRY.

BY C. W. HARRISON.

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OWING to the vast amount of research which has been done along the lines of agricultural chemistry during the last few years it has

been found impossible to cover all of the ground thoroughly, but an attempt has been made to review briefly some of the more important work and to classify this so as to show partially the advancement which has been made in this field.

Another factor which rendered anything like a complete review possible is the very close relationship which agricultural chemistry bears to agriculture and some of the other related sciences; in fact, there is no sharp dividing line, one shading off into the other so perfectly that what many authors consider in one sphere another will place in the other. Therefore, it has been decided simply to consider in this review those articles which deal primarily with subjects which obviously fall under the head of agricultural chemistry.

Following out this plan, therefore, the work has been classified under the general heads of fertilizers, soils, field crops, feeding experiments and dairying, and then these have been subdivided accordingly as the case required.

FERTILIZERS.

Phosphoric Acid.—As there seems to have been more work done on fertilizers than on any other subject this will be noticed first. Under the general head of fertilizers is included phosphates (of all kinds), potash salts, nitrates, ammonium sulphate, organic nitrogen, barnyard manure, green manuring and nitrogen derived from the air by leguminous crops. With the foregoing substances we find accounts published of almost unending numbers of pot and field experiments, which, in many cases, bring out valuable data in regard to their value in agriculture, either for some specific crop or relatively to each other.

Of the different kinds of fertilizing materials probably more work has been done on phosphates than on any other substance. A large number of experiments are reported on the relative value of phosphoric acid in the form of superphosphate, Thomas slag, bone meal and ground mineral phosphates. In general, almost all of the experimenters along this line conclude that, except on special classes of soils, superphosphates are the most valuable. In pot experiments with superphosphates bone meal and Thomas slag Rindall[1] has concluded that superphosphate has a higher value as a phosphatic fertilizer than either Thomas slag or bone meal, and that the latter two, contrary to the results of German experiments, are about equal. As regards the value of the water-insoluble phosphoric acid contained in superphosphates, Schulze[2] has shown by experiments with oats that this form has about one-third the fertilizing value of the water-soluble phosphate and this may be increased to about one-half under favorable conditions and in case there is a lack of phosphoric acid.

[1] Landtbr. Styr. Meddel., No. 44, pp. 19–28 (1903).

[2] Deut. Landw. Presse., **30**, No. 2, pp. 12–13 (1903).

As regards the action of soil moisture on the different phosphates it is stated by one investigator[1] that the moisture content of the soil does not affect the action of the phosphoric acid of bone meal, but does affect that of Thomas slag and superphosphate, the action being favored by an increase in the water content. Ullman[2] has shown that the water-soluble phosphoric acid, when applied as a top dressing, circulated in the soil and remained soluble in water for a long time, the rate of inversion being dependent on the amount of lime, magnesia, oxide of iron, etc., present, and by this method the phosphoric acid is distributed uniformly through the soil in a fine state of division and is therefore easily assimilable by the plant, and it is to this fact that many attribute its value. However, Paturel[3] has shown that in all cases this is not true, especially in light soils, having little absorptive power and poor in lime; in this case he found a portion of the superphosphate still soluble after a lapse of several months. His results show that the plants take up their phosphoric acid in a soluble form and that the soil solutions are an important factor in furnishing it. It is not, however, necessary for all the phosphoric acid to be in a state of solution as Schloesing[4] has shown by experimenting with maize grown on soils one rich and the other poor in phosphoric acid; in the rich soil containing 1,012 mg. per 36 kg., of water-soluble phosphate, the plant removed 1,115 mg., while in the poor soil containing 199 mg. the plant obtained 451 mg. This shows that the roots of the plant are able to dissolve the phosphates without the assistance of the soil water and, therefore, it is not necessary for them to be in a state entirely soluble in water. However, in soils which have no solvent power for phosphates the roots of plants exert quite a difference in degree, it having been shown that maize exerts a very great solvent action on mineral phosphates, and that in the case of beets it is very small, while leguminosae occupy an intermediate position.

Among the other causes influencing the action of phosphates the investigations of Schreiber[5] may be mentioned; these extended over a series of years and show that on acid, peaty soils Thomas slag and mineral phosphates give better results than superphosphate. On sandy soils slag seems to be more beneficial than precipitated phosphates; liming also exerts a marked influence; it reduces the action of mineral phosphates, but renders the phosphoric acid of humus soils more available. Another investigator[6] concluded, however, that slags are preferable to superphosphates on soils containing less than 3 per cent. of assimilable lime.

Slag perhaps exerts the most lasting action; by plat experiments Wagner[7] showed that it exerted an effect on grass land nine

[1] C. von Seelhorst: *Jour. Landw.*, **50**, No. 2, pp. 167-174 (1902).
[2] Abs. in *Chem. Ztg.*, **24**, (1900).
[3] *Ann. Agron.*, **28**, No. 8, pp. 385-398 (1902).
[4] *Compt. Rend.*, Acad. Sci., Paris, **34**, No. 1, pp. 53-55 (1902).
[5] Maeseyck: Vanderdonck Robyns, 1903, p. 35.
[6] E. C. Praedel: *Sta. Agron.*, Nancy, Bull. 4, pp. 15-24 (1901).
[7] *Ztschr. Landw.*, Kammer Schleisien, **8**, p. 64 (1904).

years after its application and that medium applications continuously for twelve years were beneficial. This author also states that the higher the phosphoric acid content the less will be the application of nitrogen required and the poorer the soil in calcium carbonate, iron and alumina the smaller the application of phosphoric acid required.

As to the value of bone meal as a phosphatic fertilizer, most investigators have placed it below Thomas slag. Söderbaum[1] concludes from his experiments that while under favorable conditions it may produce as good results as slag and even as superphosphate, still its action is so affected by agencies which do not affect the action of slag that greater care must be exercised in its use than in any other form of phosphates. In the majority of cases it cannot be used to advantage on soils rich in lime.

The same investigator[2] has also carried on extensive investigations as to the fertilizing value of precipitated calcium phosphate. He worked upon a poor sandy soil, making duplicate experiments, one without the addition of lime and one with it. The fertilizers used were dicalcium phosphate, prepared electrolytically from apatite; tricalcium phosphate prepared also from apatite by a different process; precipitated phosphate which was a mixture of the two and contained 41 per cent. of total and 24 per cent. of citrate-soluble phosphoric acid, steamed bone and superphosphate. The crop experimented with was oats. The results show that the favorable effect of both the precipitated phosphate and bone meal was lessened by the addition of lime, but the superphosphate was not affected by it. The conclusion is drawn that on freshly limed soils tricalcium phosphate produced somewhat better results than bone meal, and that on soils poor in lime it gave slightly lower results, and that dicalcium phosphate was about equal to superphosphate, regardless of whether the soil had been limed or not. As regards the relative amount of phosphoric acid which plants contain, several investigations[3] have been carried on, which indicate that at least some of the crops contain ammoniacal nitrogen and phosphoric acid in proportion to form ammonium magnesium phosphate. Finally, the chemical methods for the determination of the fertility of the soil with respect to phosphoric acid may be noticed. There are numerous arbitrary methods using different strength of solutions (usually about 2 per cent.) of weak acids, such as citric, acetic, etc., or solutions of acid salts such as potassium binoxalate, bitartrate, etc. These solutions have been tested by pot experiments, but on account of the fact that plants differ so much in their power of taking up phosphates from the soil, no one solvent can be relied upon to show the amount of available phosphoric acid present in the soil. Gedroitz[4] grew twelve dif-

[1] *K. Landt. Akad. Handloch Fidskr.*, **42**, No. 1, pp. 42–53 (1903).

[2] *Medd. K. Landtb. Akad. Exptlfalt*, No. 75, p. 14 (1902).

[3] H. Pellet: Abs. in *J. Chem. Soc.* (London), **82**, No. 478, II, p. 526 (1902).

[4] *Zkur. Opuitn. Agron. Jour. Expt. Landw.*, **4**, No. 4, pp. 403–432 (1903).

ferent varieties of plants on the same soil, and determined the assimilability of the phosphoric acid by means of a 2 per cent. citric acid, but found no close agreement between this and the actual amount removed by the plants. Similarly, he grew oats and mustard on the same soil, and found that they varied widely in the amount of phosphoric acid which they assimilated. He further showed that the availability of the phosphates of the soil as determined by the 2 per cent. citric and acetic acid solutions was, beginning with the highest, first calcium, second aluminum, and third iron phosphates, while the relative assimilability as determined by growing crops of flax, oats and mustard on this soil was first aluminum, second calcium, and third iron phosphate.

It may, therefore, be seen that thus far there has been no satisfactory method proposed for determining this important point.

Potash.—Taking up next the subject of potash, it appears that there has not been very much work done along this line, and comparatively few points of special interest or value brought out. While it is true, that in a majority of fertilizer experiments potash has been applied, still in the majority of cases it was the nitrogen or phosphoric acid that was being studied and not the potash, it being simply added to complete the fertility of the soil. There have been a considerable number of experiments carried on in attempts to substitute soda for potash, but these have not been attended with any great degree of success. Doll[1] grew barley in pots containing soil composed of one-third sandy field soil and two-thirds pure river sand, and fertilized with sulphates and chlorides of sodium and potassium singly and combined. The chlorides gave better results in each case than the sulphates. This is thought to be due to the greater diffusibility in the case of potassium, and to the rendering of the potash of the soil available by the sodium. The best results were obtained with mixtures of the two salts, but applications of soda were less effective than potash. Analysis of the crop showed that an increase in the crop was accompanied by an increase in the proportion of potash or soda in the plant.

As regards the value of the different potash salts, quite a number of investigations have been carried on to test the relative value of 40 per cent. potash salt as compared with kainit. The 40 per cent. salt is prepared from carnallit by concentration. Coöperative[2] experiments lasting for two years were carried on by a number of German experiment stations using the 40 per cent. salt and kainit. The conclusion is reached that kainit gave better results on cereals on either light or heavy soils, and there was no injurious effect on the mechanical condition of the soil attending its use. The 40 per cent. salt produced a greater yield of potatoes both of total crop and of starch than kainit. The two salts were about

[1] *Landw. Vers. Stat.*, **57**, No. 5-6, pp. 471-476 (1902).

[2] M. Maercker and Schneidewind: Abs. in *Chem. Zlg.*, **26**, No. 16, p. 53 (1902).

equally effective on sugar-beets, both increasing the sugar content. It is pointed out, however, that the 40 per cent. salt may be better for this crop because it can be used in larger quantities without danger of injuring the mechanical condition of the soil. Bachmann[1] reports results somewhat different from these, he applied the 40 per cent. salt to oats in the spring and got a larger increase in grain and less in straw than with kainit. He also used lime in these experiments, but it did not change the relative results.

Kainit gave better results on sugar-beets than the 40 per cent. salt, if applied in the fall, but was the less effective of the two if applied in the spring. From the financial standpoint the kainit gave the better results and in every case gave the greater residual effect. Schulze[2] carried on experiments for two years on oats and barley to test the relative value of kainit, muriate and sulphate of potash; muriate stood first in regard to both yield and utilization by the crop; sulphate was second in the yield of crop produced but third in regard to the utilization of the potash by the crop.

The effect of potash on the form and composition of the plant has been studied by a number of investigators. The article[3] entitled "The Effect of Potash on Plants as Shown in Experiments with Potatoes, Tobacco, Buckwheat, Mustard, Chicory and Oats" presents some interesting data along this line. The experiments were carried on for several years, using a soil mixture almost free from potash. The potash applications were more effective in increasing the size of the plant organ containing the reserve material than in increasing the yield of leaves and stem; this was especially noticeable in the case of the beets and potatoes. By decreasing the amount of potash a similar diminution was noticed in the percentage of stem and leaves, but not in the per cent. of roots. The effect of potash on the appearance of the plant was quite noticeable, the lack of this substance producing a yellow-brown color of the leaf, with spots of a similar color, but more intense, and in some cases assuming a whitish appearance; these spots appeared between the veins while the ribs retained their dark green color. These symptoms were especially noticeable in the leaves of tobacco, potatoes and buckwheat. When there was a lack of potash in the soil this was shown by a characteristic curling up of the leaves and a collapse of the plant. When nitrogen and phosphoric acid were deficient in the soil it affected the plant quite differently. The lack of phosphoric acid showed itself by a dark green coloration of the leaves, while an insufficient supply of nitrogen produced a yellow-colored leaf. When there was a lack of potash, a heavy

[1] *Deut. Landw. Presse*, **30**, No. 15, p. 120 (1903).

[2] *Jahresber. Thät Agr. Chem. Vers. Stat.*, 1901–2, pp. 21–32.

[3] H. Wilforth and G. Wimmer: *Arb. Deut. Landw. Gesell.*, No. 68, pp. 106 (1902). Abs. in Expt. Sta. Record, Vol. XV, No. 3, p. 235.

application of nitrogen reduced the relative yield of tubers, and also the percentage of starch, this being noticed in the case of beets and potatoes where an experiment was run under the same condition, but using a small application of potash.

A study was also made of the amount of water transpired per gram of dry matter produced. An application of potash increased this; this the author believes to be due to the check in growth when the supply of potash is used up, as in that case the transpiration continues while the production of dry matter stops. For each gram of dry matter produced it was found that the tobacco transpired 300 grams, potato 200, and oats 460. With the exception of the potassium nitrate, there was no great difference in the effect of the different salts used. On the potatoes potassium sulphate and chloride gave practically equal yields, but the sulphate produced the higher percentage of starch. It was found that for each gram of potash taken up, potatoes produced 36 grams, and oats 29 grams of starch. The content of sugar in the beets was also very much affected, being 8 grams of sugar per gram of potash taken up, when there was no potash added, and 25 grams when there was a large amount of potash present.

As regards the manner of applying potash salts, most authors[1] favor top dressing, this being shown especially in the case of winter grain, where the weather conditions were well suited to dissolve and distribute the salt in the soil. It has also been pointed out that they should not be applied when the plants are moist with dew or rain, since they tend to stick to and injure the leaves. Therefore, the best results are generally obtained by applying the salt in dry weather just before a rain.

Finally, the point brought out by Bolin[2] should be noticed. In coöperative experiments with barley and oats, using different mixtures of fertilizers, it was shown that fertilization with nitrogen and phosphoric acid, on an average, gave a smaller increase in the weight of kernels than the nitrogen and potash fertilizer, which indicates that the potash has at least as much effect on the seed formation as the phosphoric acid. Noticing now the nitrogenous fertilizers, namely, nitrate of soda and sulphate of ammonia, it has been found that considerable work has been done comparing the relative value of these two. Bachmann,[3] for instance, in working on different kinds of plants, concludes that if ammonium sulphate is applied in the proper time and manner, it will give often better results than nitrate of soda, and he shows that Wagner's ratio of 100 : 90 is not correct. He found early spring applications most effective with most crops, and also that a considerable after-effect was exerted, which was not the case with the nitrate of soda.

[1] Bachmann: *Deut. Landw. Presse.*, **29**, No. 97, pp. 735–6 (1902).

[2] *K. Landt. Akad. Handl. Och Tidskr.*, 1903, p. 133.

[3] Fühlings: *Landw. Ztg.*, **52**, No. 4, pp. 132–138, No. 5, pp. 183–190 (1903).

Another author[1] reached quite a different conclusion in that he finds Wagner's figures too high; he places the effectiveness of sulphate at 86 per cent., which falls to 80 per cent. in soils poor in lime, and to 63 per cent. in soils very rich in lime. According to the results of Wagner,[2] 100 parts of ammoniacal nitrogen yielded 93 parts of nitric nitrogen in the soil. These experiments consisted of a number of coöperative experiments carried on at different German stations. On the average, the crop used the nitrogenous fertilizers in the following order: nitrate of soda, 100; sulphate of ammonia, 94. With oats the ammonium salts were 98 per cent. as effective as the nitrate of soda. However, in field experiments with a number of different crops, the sulphate of ammonia only showed an effectiveness of 70 : 100 compared with sodium nitrate; this the author attributes to the loss of nitrogen in the form of ammonia. It was also found that soda increased the yield, but the continued use of sodium salts is cautioned against as being injurious to the physical properties of the soil.

The action of sodium nitrate on the physical properties of the soil was studied at Rothamstead,[3] where it was discovered that the plats on which sodium nitrate had been added did not contain the very fine particles which were found in adjoining plats to which there had been no sodium nitrate added.

This was especially noticeable in the mangle field where there had been continued cultivation, but was not noticed on grass fields where the sod protected the ground from washing. This the author attributes to the deflocculation by the sodium nitrate, and the washing of the finer particles into the subsoil. Analysis of the soil supported this view in that the finer particles of the subsoil were richer under the plat to which the nitrate had been added, and the condition of the soil showed every indication of deflocculation.

As has been pointed out in discussing potash, a deficiency of nitrogen in the soil manifests itself by the plant becoming a light green or yellowish, changing finally to a light, brownish yellow color.

Nitrogen.—The action of nitrate nitrogen is decidedly affected by large quantities of organic matter, being diminished considerably by applications of straw, peat, etc. Lastly, it has been noticed that nitrates tend to increase the period of growth and retard ripening; therefore, great care must be exercised in applying it to late crops. It is also much quicker in its action than sulphate of ammonia, but it is not fixed by the soil, and unless the crop is growing rapidly there is great danger of it being washed out by rain and lost. If, however, the conditions are unfavorable for nitrification it will usually prove more effective than sulphate

[1] S. Gradeaw: *Jour. Agr. Prat.*, N. Ser. 5, No. 10, pp. 308–309 (1903).

[2] *Arb. Deut. Landw. Gesell.*, No. 80, pp. 340 (1903).

[3] A. D. Hall: *J. Chem. Soc.* (London), **85**, No. 501, pp. 964–71 (1904).

of ammonia, since only certain plants have the power of taking up ammonium salts. It is also stated[1] that commercial sodium nitrate always contains chlorates and perchlorates of sodium and potassium; since both of these are injurious to plants, it may be that some of the bad effects reported in the use of sodium nitrate may have been due to the presence of these substances.

A large amount of the work which has been done on barnyard manure has been in trying to devise a suitable method of preserving it so as to prevent loss of nitrogen. These methods have been of both physical and chemical nature, using chemicals such as lime, gypsum, superphosphate, sulphuric acid, etc., and also by storing in heaps and similar physical means.

Most authors[2] conclude that sulphuric acid is the most effective preservative, since it entirely prevents the loss of nitrogen, but it also has the disadvantage of being difficult to obtain, dangerous to handle, and also it imparts an acid reaction to the manure.

Lime, calcium, carbonate, gypsum and superphosphate are all very uncertain in their action, at times giving good results.

Schneidewind[3] has concluded that sulphuric acid effectually prevents loss of nitrogen, but it also interferes with the decomposition of the manure. He also states that the preservative materials such as gypsum, lime, copper sulphate, etc., are useless, and that peat and earth are the most satisfactory preservatives that can be used.

The storage in heaps, whether loose or packed, has also proved very unsatisfactory, since a large loss of nitrogen occurs, especially in the early stages of the storage.

As regards the fertilizing value of barnyard manure it is generally concluded that owing to its physical action on the soil it will often produce effective results where commercial fertilizers fail. In one case[4] it has been shown that the maximum yield of root crops was only obtained by an application of barnyard manure in conjuncture with commercial fertilizers, this being attributed to the physical action, since even with a heavy application of nitrate of soda the quantity of nitrogen taken up was increased by an application of barnyard manure. A larger yield of potatoes and turnips was also produced by a heavy application of barnyard manure than by the application of a complete commercial fertilizer.

In comparing[5] the deep stall manure with the barnyard manure it was found that the former gave larger yields than the latter, but the yield was not in proportion to the larger quantity of soluble nitrogen which it contained. It is also noticed that the stall manure suffered greater loss when spread on the field than did

[1] H. Pellet and G. Fribourg: *Ann. Sci. Agron.*, No. 2, pp. 199–225.

[2] J. Sebelien and E. Forfang: *Norsk Landmandsblad.*, **23**, No. 11, p. 135 (1904).

[3] *Oesterr. Chem. Ztg.*, **6**, No. 18, p. 412 (1903).

[4] M. Gerlach: Abs. in *Chem. Centrbl.*, II, No. 11, p. 764 (1902).

[5] W. Schneidewind, D. Meyer and W. Gröbler: Landw. Jahrb., **31**, Nos. 5 and 6, pp. 826–908, 963–968 (1902).

the barnyard manure, and, therefore, it should only be supplied in quantities sufficient to furnish the crop.

On soils[1] poor in nitrogen, liquid manure, when applied alone, gave larger yields than when used in conjuncture with fresh manure and straw. This is believed to be due to the fact that fresh organic substances furnish food for certain soil bacteria which withdraw the nitrogen from the use of the plant, and this results in a diminished yield on soils deficient in nitrogen. However, on soils rich in nitrogen the manure did not decrease the yield, since here there was a plentiful supply for the denitrifying bacteria, and also for the crop.

Noticing now the work on green manuring, the principal crops which have been used for this work are peas, beans, vetches, clover, alfalfa, buckwheat, etc. It is generally concluded that beans and peas produce the best results. Green manuring generally exerted an effect for about two years, and finally disappears about the third year.

For preserving[1] the nitrogen of the soil during the fall months the legumins are generally considered the best, since they not only preserved the soil nitrogen, but also added a supply from the air. Some authors place their value as nitrogen furnisher at about 40 per cent. compared with nitrate of soda. The practice of green manuring for sugar-beets is said to decrease their quality, but this is more than made up by the increase in the total crop.

As regards the fixation of atmospheric nitrogen by the bacteria of the soil, many varieties have been separated and while most of these when grown in the proper media, and usually with the addition of grape-sugar, have the power of assimilating nitrogen, still when they are applied to the soil they do not seem to produce any favorable effect on the crop; in fact, many investigators have procured a decrease in the crop by inoculating the soil with them. Whether this is due to symbiosis or not has not yet been proved. The nitrates of the soil also affect the assimilation of free nitrogen, the assimilation increasing as the amount of nitrates decreases.

Bonnema,[2] however, has advanced the theory that the assimilation of free nitrogen is a chemical process and not due to bacteria. He calls attention to the iron content of the root tubercles of leguminous plants and from this he believes that there is a considerable amount of iron hydroxide present which is essential to the process of assimilation of nitrogen by the bacteria. Denitrifying organisms also occur in the soil, which have the power of reducing nitrates, and these organisms also occur in horse manure and straw. Klyncharev[3] has studied the effect of bringing solutions of nitrates

[1] W. Schneidewind: *Landw. Jahrb.*, **31**, Nos. 5 and 6, p. 826 (1902). Abs. in Expt. Sta. Rec., Vol. XIV, No. 9, p. 852.

[2] Tiddskr. Landbr. Planteavl, **5** (1859).

[3] *Chem. Ztg.*, **27**, No. 67, pp. 825–826 (1903).

[4] Izv. Moscow. Khoz. Inst. Ann. Inst. Agron. Moscow, **8**, No. 2, pp. 107–149 (1902). Abs. in Expt. Sta. Record, Vol. —, No. —, p. —.

into contact with soil in cylinders. He concluded that the rate of denitrification was dependent on the amount of organic matter (such as starch) present in the soil.

Lastly, the other form of atmospheric nitrogen, *viz.*, the so-called lime nitrogen, has so far not come into extensive use, but may in the future play an important rôle in agriculture.

This substance is cyanamide and it is formed from calcium carbide in the manufacture of acetylene gas; it contains about 15 to 25 per cent. of nitrogen. Earlier experiments[1] with this substance as a fertilizer placed its value as a nitrogen furnisher nearly as high as nitrate of soda, but more recent investigators have found this figure to be too high and that it possesses only about three-fourths the value of nitrogen in the form of nitrates. It has also been found to give better results when applied late rather than early, and that on certain classes of soils it has an injurious effect, due, it is thought, to the formation of dicyandiamide which apparently is poisonous to plants. It is, however, a quick-acting fertilizer.

Lime.—In concluding the subject of fertilizers lime will be noticed briefly. As a fertilizer the action of lime is generally admitted to be indirect, since there are few soils which do not contain a sufficient supply to furnish the needs of the plant. In acid clayey soils it nearly always proves effective. It has also been found to increase nitrification. Ulbricht[2] reports results of experiments on barley, using lime fertilizers, which produce a marked increase; however, by applying lime in February he reduced the weight of grain. The use of lime and magnesia increased the tilling of the grain. Heavy applications of lime with small magnesia content increased the entire growth, but of straw more than of grain, the weight of the grain was also less. The action of lime is also believed to be due to the neutralizing of the injurious effect of magnesia. The ratio which the lime in the soil should bear to the magnesia has been also extensively studied.

Some authors place the lime magnesia ratio at about 3 : 1 for crops which have an abundant leaf production, while for cereals about 1 : 1 gives the best results.

SOILS.

Taking up next the subject of soils, it is noticed that there are numbers of analyses published, including every variety of soil. These have been both physical and chemical and generally with a view of establishing a method whereby the fertilizer requirements of the soil may be ascertained or the available fertilizing ingredients determined. Besides this there has been a large amount of work done on the soil temperature, moisture content, humus content, soil solutions, etc.

[1] *Mitt. Deut. Landw. Gesell.*, **19**, No. 8, pp. 45–46 (1904).

[2] *Landw. Vers. Stat.*, **57**, No. 1–2, pp. 103–166 (1902).

In studying the water content of the soil Tretyakov[1] has shown that under papilionaceous plants the moisture content is 0.32 per cent. lower than under graminaceous plants. This is believed to be due to unequal root development of the two families. He also showed that an alfalfa field ploughed up in the fall, winter or spring contained more moisture than those remaining under the alfalfa. Deep ploughing also increased the moisture content, which was noticeable for three years.

Barnyard manure exerted a favorable influence on the moisture content, which was also noticeable for several years. Another author,[2] in studying the evaporation of water by wheat as affected by fertilizing and the different moisture content of the soil, has shown that a high moisture content increases the effect of fertilizing. He also showed that when the moisture content was small, water was evaporated at the rate of 500 units of water per unit of yield. In cases of large moisture content tilling began earlier and the straw and root developed more strongly, while the head became shorter.

The consumption of soil moisture by different crops is also quite different. Von Seelhorst[3] studied a variety of plants and found that rye drew less moisture than wheat, clover left the soil very poor in moisture, while peas and potatoes left the soil very moist.

He concludes that there is a close relation between the yield and growth of individual plants and the water content of the soil.

As to the composition of the different particles of the soil, Rudzinski[4] has reported quite a lengthy work on this subject. By mechanical analysis he separated the different soil particles and studied their relative fertility. He mixed the different particles with sand and grew oats, also using check experiments applying fertilizers. He concluded that the total content of nitrogen, phosphoric acid and potash in the mechanical elements of the soil investigated decreased with an increase in their size; however, assimilable substances for the plant are contained in both the silt and the coarser particles, and since the finer particles are present in small quantities in most soils, the fertility of the soil must depend largely on the coarser particles.

He states finally that it is impossible to judge of the fertility of a soil from its mechanical composition, since the particles of soils, even of like geological origin, are unlike in chemical composition.

Of the methods of soil analysis perhaps the most reliable for determining the fertilizer requirements of the soil is the so-called

[1] Pochvovedenie: *La Pedologie*, **4**, No. 3, 219-234; **4**, 378-392 (1902).

[2] Yanovchik: *Kherson*, **9**, pp. 142 (1902).

[3] *Jour. Landw.*, **50**, No. 2, pp. 151-164 (1902).

[4] Izv. Moscow. Selsk. Khoz. Inst. Ann. Inst. Agron. Moscow, **9**, No. 2, pp. 172-234 (1903); Abs. in E. S. R., Vol. XVI, No. 4, p. 345.

physiological analysis. Vanderyst[1] has defined this as follows: Physiological analysis of the soil consists of two or more comparative synthetic culture experiments, executed systematically with one or more species of cultivated plants, in a soil modified in various suitable ways by simple and chemically pure fertilizers with the object of determining, on the basis of the examination of the plants and the quality, quantity and mineral composition of the crop produced, the one or more necessary or useful fertilizing elements which are required by the one or more species of plant experimented with, under the conditions of environment in which the experiment is made. This, the author points out, differs materially from fertilizer experiments, but he also shows that this method should be supplemented by fertilizer trials. He also points out that this method is very faulty, owing to the large number of factors which may affect the results, some of which are the variability of the mineral composition of the plant with an excess of some one ingredient, the physical action of the fertilizer on the soil, the difference in solubility, etc. He further points out that chemical analysis only shows the percentage composition of the soil, but cannot be relied upon to show the availability. It may, however, be of great value in showing the nature and total quantity of elements necessary and the existence of useful, indifferent or poisonous substances which may be present.

As to the bacteriological character of the soil quite a large quantity of work has been done, but as yet the data on the subject is of a very uncertain nature, and a large part of it is conflicting.

FIELD CROPS.

Taking up next the field crops and noticing briefly a few of the most important of these we find that:

Of the cereals, more work has been done on wheat than on any of the others. The investigation has been chiefly along the lines of fertilizing, variety tests, effect of environment, composition and in combating diseases, chiefly smut.

As regards the fertilizer experiments, there do not seem to have been any points of special interest brought out, since most of them are of local importance only. Nitrogen[2] has been shown to lengthen the lower internodes and shorten relatively the upper ones, and nitrate of soda produced this more than sulphate of ammonia. This increases the tendency to lodge. Ammonia also produces a stronger plant and also seems often to produce a better quality of grain, though, as a rule, the yield is not as large as with nitrate.

The composition of the wheat has also been extensively studied. Starch[3] has been shown to come from the stem into the head of

[1] *Rev. Gen. Agron. Louvain.*, **11**, No. 9, pp. 410–412 (1902); Abs. in E. S. R., Vol. XV, No. 8, p. 757.

[2] H. Claussen: *Jour. Landw.*, **49**, No. 4, pp. 365–388 (1902).

[3] Deherain and Dupont: *Ann. Agron.*, **28**, No. 10, pp. 522–527 (1902).

cereals, and does not gather in the leaves as it does in the other plants.

There have been quite extensive studies made of the nitrogenous bodies in wheat. Gliadin and glutarine are the most important; these substances exert a great effect on the baking quality of the flower. They are not generally thought to be formed from the same substance nor to have the same composition. In the unripe grain the nitrogenous bodies are mostly soluble, and the process seems to consist of a change from soluble to solid and stationary bodies, the amido bodies going over into albumen.

As to the work on cereal diseases, this has been principally in attempting to obtain a satisfactory method of preventing smut. Many different chemicals have been used on the seed, including copper sulphate, corrosive sublimate, formalin, etc.; hot water has also been used, but these have only been partly successful. It has also been suggested that by studying the effect of soils, fertilizers, exposure, etc., in all countries on cereal rusts, it may be possible to breed a more rust-resistant variety.

One other point in cereals is the relation of the mineral matter in the stem to lodging. The results of Lienan[1] point to the fact that there is a close relation between the mineral fertilizers added and the thickness of the cell walls, as well as to the amount of total ash in the stem. Phosphoric acid was very marked in producing thick walls, but this effect was lessened by applications of lime or potash at the same time. Potash increased the size of the cell lumen, as did also nitrogen, which also reduced the thickness of the cell walls; however, a large application of phosphoric acid at the same time counteracted this. Ammoniacal nitrogen weakened the stems less than nitrate. Liming also weakened the cell walls.

Analysis indicated that phosphoric acid had a tendency towards decreasing the total ash and some of its components, while nitrogen, potash and lime had an opposite effect. It also seemed that the thickness of the cell walls was inversely proportional to the total ash content. The author points out that when it is necessary to add large quantities of lime or nitrogen, a larger application of phosphoric acid should also be used to counteract the tendency towards lodging which these produce by weakening the stems.

The root crops have been the subject of larger numbers of fertilizer experiments, including the effect of different fertilizers on the growth and quantity of the crop. Among this class of experiments may be mentioned the effect of chlorine on the starch content of the potato, and the influence of fertilizers on the sugar content of the beet.

Chlorides[2] have been shown to lower the starch content. Potash has been shown to increase both the quantity and quality, while phosphoric acid exerts a detrimental effect on the crop and

[1] Inaug. Diss. Univ. Königsberg, 1903, p. 91.

[2] *Jour. Landw.*, **47** (1899).

produces an abnormal leaf and stem development. It is also true that the leaves of potatoes rich in starch contain more phosphoric acid and potash than those poor in starch.

With sugar-beets[1] it is noticed that insufficient potash decreases the sugar content, while a large quantity of nitrogen exerts a similar effect and also seems to produce a tendency towards disease, while a small quantity of nitrogen, under similar circumstances, produces a larger and healthier crop; used in connection with phosphoric acid the effect is not so marked; a lack of potash increases the growth of leaves, while a subnormal quantity of phosphoric acid produces a beet with a fair sugar content and a subnormal quantity of nitrogen produces one of very high sugar content. The leguminous crops have been studied quite extensively, both as a means of furnishing nitrogen and from a bacteriological standpoint, numerous experiments being carried on in inoculating the soil with various kinds of bacteria and testing their effect on the leguminous crops.

Another branch of agricultural chemistry which has received considerable attention is that dealing with seeds, principally their selection and germination. The influence of temperature on germination is very important, an elevated temperature producing quick germination, but the root system being small and the roots themselves having but few branches. It has also been noticed that many seeds can stand a high temperature for a short time and still retain the power of germination; if, however, they be heated long they lose this power. Seeds have been found which would germinate after being heated one hour at a temperature of 110 to 120, but if heated several days at from 95 to 97 they were killed.

Other important factors in germination, such as the effect of moisture, sunlight and age, have all received considerable attention.

The weed problem is another one which is being extensively studied. Many experiments have been carried on in attempts to produce methods by which objectionable weeds might be eradicated. It has been pointed out that both the yield and money value of crops is very seriously affected by weeds. Korsmo[2] investigated the effect of weeds on the value of several different crops, in which he calculated a loss of about 47 per cent. in money value.

Spraying with different chemicals, such as copper sulphate, has been tried quite extensively in weed eradication, but with doubtful results.

DAIRYING.

The subject of dairying will only be noticed very briefly. The

[1] *Deut. Landw. Presse.*, **29**, No. 11, p. 84 (1902).

[2] Tidsskr Norske Landbr., **10**, No. 6, pp. 247-280; No. 7, pp. 295-330 (1903).

work along this line has been largely in testing the effect of different feeds on the quantity and quality of the milk and butter. Besides this the bacteriology of milk and butter has been largely worked upon.

The kind of food seems to exert a direct influence on the butter; this has been noticed in the case of cows fed cotton seed cake, when the butter gave the Halphen reaction. In fact, it seems that some of the fat passes through the body into the milk without undergoing any change, it having been noticed that some of the constants for the butter vary exactly with those of the fat fed. The quantity of volatile fatty acids in the butter also changes with a change in ration, but whether this is due to the change in food or in nutrition has not been definitely decided. The food also affects the secretion of milk, but the general conclusions are that while different food-stuffs exert a specific influence outside of their food value, this is not constant with different animals and therefore no feeding-stuff has money value higher than its food value.

As regards the quality of the milk as affected by inequalities in the intervals of milking this seems to be slight and of little importance.

FEEDING EXPERIMENTS.

Taking up lastly the feeding experiments, it is noticed that these are not so extensive as are carried on at home. Sugar-beets and other root crops have been tested considerably as foods and also in comparison with grain and oil cakes, it having been shown that an equal quantity of dry matter in root crops is about equal in value to grain. Sugar-beets have proved a fairly good feed, but they are generally concluded not to be as good as mangles. For milch cows they are said to give good results by increasing the milk flow and not decreasing its quality. Molasses has also given fairly good results, it having been found that by using bagasse as an absorptive a food can be made that contains 70 per cent. of digestible carbohydrates.

The character of the fat in the body of the animals is affected by feed, palm-nut cake having been shown toproduce hard fat.

No very important work seems to have been done on the concentrated foods. They are usually reported as giving good results and many of the authors advise more their use in place of the common food mixtures. The digestibility of cellulose and pentosans has been a subject for considerable study. The digestibility of pentosans is said to be parallel to, and vary directly with, that of carbohydrate. Cellulose seems not to exert any influence on the cleavage of protein. It does, however, protect fat and may therefore be called a nutrient.

BUREAU OF CHEMISTRY,
DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

NOTES ON THE USE OF RARE EARTHS IN ELECTRIC ILLUMINANTS.[1]

By Murray Charles Beebe.

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As scientists and engineers have come to a realization of the inefficiency of existing methods of illumination, the problem of improving upon these inefficient methods has received considerable attention. While the element carbon has heretofore been almost exclusively used commercially in both arc and incandescent lamps, the rare earth oxides, so-called, have recently been found to possess desirable properties for use as illuminants.

We are already familiar with the work of Auer von Welsbach in producing gas mantles of thoria and ceria. To use the rare earths in electric illuminants was a logical step. However, the problem presented difficulties not encountered in the production of a serviceable gas mantle. We should remember that an illuminant, to be an improvement over the Edison or carbon filament lamp in the matter of efficiency, must be capable of withstanding a higher temperature than the carbon filament for a length of time sufficient to make it commercially attractive. One might at first suppose that it would be difficult to improve upon the carbon filament in the matter of efficiency, or the ability of the filament to operate commercially at a very high temperature, since carbon is practically infusible and the rare earths are fusible and in a carbon arc. Carbon, however, slowly vaporizes at the temperature at which it operates in the incandescent lamp and, finally, after 400 to 600 hours has depreciated in light giving power to such an extent that it is best to replace it. It is the vaporizing properties rather than the melting-points of the materials with which we are concerned in this problem. It has long been known that substances which are commonly regarded as insulators, such as glass and porcelain, become quite good conductors of electricity at higher temperatures.

Prof. Buff, in 1854, read a paper "On the Conductivity of Heated Glass for Electricity," and Faraday's "Researches" give a number of examples of such conductors. Jablochkoff attempted to use refractory materials, such as lime, to separate and insulate the carbon electrodes of his Jablochkoff candle. He soon found that these supposed insulators in reality became conductors and emitted light by virtue of the current passing through them from one electrode to another. He even designed terminals with which to carry the current of electricity to the lime conductor, with the idea of making a lamp based on this principle. It is safe to say that had it been possible to produce electricity as cheaply then as now, lamps of the Nernst type would have been known commer-

[1] Read before the Pittsburg Section of the American Chemical Society, March 23, 1905.

cially much sooner than they were, for Jablochkoff's persistent attempts at commercial exploitation were baffled largely by the undeveloped state of electrical engineering.

That the rare earth oxides are exceedingly refractory and do not readily vaporize at a high temperature, makes the Welsbach mantle possible; that these oxides will conduct electricity when hot, makes the Nernst lamp possible. Of all the oxides which conduct electricity but few are refractory enough for an efficient filament of glower. It was in determining the most desirable of these and in fixing the best proportions to use that Nernst did his greatest work.

Ordinary red iron oxide, when formed into filaments and baked, will conduct electricity at ordinary temperatures, but such filaments do not withstand sufficiently high temperatures to be used as light sources. Magnesia and thoria, on the other hand, withstand exceedingly high temperatures, but these conduct electricity only with great difficulty. In general, mixtures of two or more oxides conduct better than a single oxide and, in turn, the fusing-point of the mixture is lower than that of either oxide alone. It seems that the vaporizing point is not necessarily lowered, judging from the fact that thoria and the small amount of ceria used in a Welsbach mantle form quite a stable mixture, or possibly a chemical combination, while ceria alone or uncombined is a somewhat undesirable oxide from its rather marked tendency to vaporize.

It would be a long story to take up the various properties of all the rare earth oxides and the possible combinations with one or more of the others. A mixture which is used largely in lamps of the Nernst type, is composed of 85 per cent. zirconium oxide to 15 per cent. of yttria earths. Zirconium is not properly classified among the rare earths, though it is customary to do so. The term "yttria," as used here, means in reality a mixture of many oxides occurring together in certain minerals and closely allied in physical and chemical properties. Zirconia was used in comparatively large quantities for the first Welsbach mantles and, hence, considerable attention had been given to various methods of producing it for such use. While many of the experimental glowers were made from zirconia bought from chemical supply houses, it was impossible to obtain uniform results from such material. Good zircon ore, which is a zirconium silicate, occurs in abundance in Henderson County, North Carolina, and this ore contains about 67 per cent. of zirconium as oxide. By treating this ore in the following manner quite uniform results are possible:

The ore is ground very fine in a ball mill and mixed with twice its weight of crude acid potassium fluoride. This is placed in an ordinary graphite crucible and heated slowly until thoroughly fused, and the ore is completely dissolved. The fused mass is then ground and dissolved in hot water containing a quantity of

crude hydrofluoric acid equal to about one-tenth the weight of the fused mass. The silica remains undissolved as potassium silico-fluoride (K_2SiFl_6) and the potassium zirconium fluoride (K_2ZrFl_6) is drained off while boiling hot into a silver-lined vessel. Upon cooling, the filtrate develops crystals of potassium zirconium fluoride and, doubtless, small quantities of other elements in similar crystal form. Iron and many other impurities which are present in the ore, or have been introduced by the use of the crude reagents, remain in the liquor which is drained from the crystals. The crystallizing process may be much hastened by artificial cooling. Rinsing the crystals with cold water is likewise beneficial in removing all traces of the mother-liquor. The crystals are gathered and fused in a platinum dish. By this means any silica present seems to be vaporized and other impurities, like titanium, are made insoluble. The fused mass is ground and dissolved in hot water and crystallized as before. A few of the first crystals are removed, or, instead, alcohol may be added to the solution until a small amount of crystalline precipitate is formed. These first crystals contain much of the undesirable impurities. They are, therefore, removed and the crystallizing process is continued. The pure crystals are then dissolved in hot water and the solution is made rather acid by the addition of pure hydrofluoric acid. Ammonia is now carefully added to the hot solution until a small amount of precipitate is formed. If the solution of the crystals has been made acid, the addition of ammonia, even until alkaline, will precipitate iron and some other foreign metals, but will leave the zirconia in solution until it is cooled and diluted.

This method was found to be an exceedingly simple one for removing iron from zirconia, which, by other methods is a troublesome operation. The hot filtrate, after removing the precipitate of iron, is dropped directly into a cold ammonia solution which at once precipitates zirconia as a hydroxide. Up to this stage of the process it has been necessary to use vessels and utensils not affected by hydrofluoric acid. The last precipitation may be made in glass or wooden receptacles. The precipitate is washed several times by decantation, and then pressed out on suction filters and, after a thorough drying by heat, is powdered and sifted through fine bolting-cloth and is then ignited in a platinum dish with a very gradually increasing temperature and with constant stirring. The ignition process requires several hours, or sometimes days, the final temperature being a good red heat. Traces of silica are removed by this operation.

The physical condition of the precipitate is dependent to a great extent upon the amount of hydrofluoric acid in excess. When precipitated from an almost neutral solution the precipitate dries into hard pieces translucent in appearance, and which are difficult to pulverize. With the greater excess of acid the material dries in

lumps resembling starch, in which condition it is much more suited to our purpose.

The zirconium made by this process seems to be reasonably pure. Precautions must be taken to keep out dirt and to that end it has been found advantageous to purify the air admitted to the rooms where the glower materials are prepared by passing it through a water spray. An absolutely pure zirconia is not required and though a trace of silica improves the efficiency and seems to diminish the initial depreciation of candle-power of a glower, it is a dangerous element to have present, for slightly more than a trace will cause a rapid change in potential difference at the glower terminals besides causing lack of uniformity in the behavior of glowers of one batch, due to the fact that the silica becomes unevenly distributed among the glowers by vaporization and condensation occurring in a roasting process, which will be described later.

Although the purest materials make the best glowers for direct current, it cannot be said that an absolutely pure zirconia is desirable for alternating current glowers. Silica is particularly undesirable in direct current glowers. In general, a glower which operates well on direct current, showing almost no change in potential difference, will show a greater change when operated upon an alternating current circuit.

The purity of the zirconia may be controlled, to some extent, by the number of times the material is crystallized during the purifying process, though each operation is attended with some loss of material. Physical properties are quite as important as chemical properties and the procedure above described was evolved to give proper physical, as well as chemical, properties to the material.

After all—"Handsome is as handsome does"—and the real test for the glower material lies in its ability to make good glowers. Test glowers have been made from hundreds of lots of zirconia and these, together with careful chemical records of each lot, have been the guide in developing the chemical process necessary for the production of good glowers. For direct current glowers a crystallizing process is also considerably used, but from a solution of zirconia in hot dilute hydrochloric acid. After two or three such crystallizations it is necessary to precipitate from a hydrofluoric acid solution, as in the first process, to get the material into proper physical shape.

As to the yttria used, this is principally obtained from the minerals gadolinite or yttrialite. Gadolinite is found in Norway and Sweden, and also in Llano County, Texas. The Texas deposit seems to be confined in a very small district and there is every evidence that it is a result of a volcanic eruption. It is found in crystalline form associated with yttrialite, cyrtolite, fergusonite, rowlandite, allanite, and other minerals. The ores from the Llano County

district are radioactive and the presence of a pocket in the quartz is generally indicated by bluish discolorations radiating from the pocket through some distance of the surrounding quartz. It is also claimed that the ores contain small quantities of confined helium gas. Gadolinite contains, roughly, 42 to 45 per cent. of yttria earths, 23 per cent. of silica, 13 per cent. iron as oxide, and 9 to 12 per cent. of beryllia. Yttrialite contains 43 to 47 per cent. yttria earths, 30 per cent. silica, 5 to 6 per cent. ceria, didymia, and lanthan, as well as small percentages of urania. Fergusonite contains 32 to 42 per cent. yttria earths and 32 to 46 per cent. columbic oxide. Rowlandite contains 47 to 62 per cent. yttria earths, 26 per cent. silica, and small percentages of iron and magnesia. Allanite contains 20 per cent. ceria and dydymia, with a small percentage of yttria earths and considerable percentages of iron, calcium and aluminum.

It is a comparatively simple matter to obtain and purify the yttria earths from gadolinite and yttrialite so that they are suitable for glower-making. About 1,000 grams of ground ore are dissolved in crude aqua regia. The residue is filtered off and the solution evaporated to dryness, repeating this operation several times, or until all silica is removed. The neutral solution is then diluted to several liters and the addition of a hot solution of oxalic acid to the hot solution containing the earths brings down the rare earths as oxalates, leaving iron and other impurities in solution. The oxalate is washed thoroughly with hot water and ignited, and the crude yttria earths are dissolved in dilute hydrochloric acid, just sufficient in amount to dissolve the oxide. To the rather dilute and neutral solution, which is cold, crystals of potassium sulphate are added in excess. After standing twenty-four hours the cerium group has been quite thoroughly separated as double sulphates and the filtrate is then treated with ammonia to bring down the hydroxides of the rare earths, thus freeing them of the great excess of potassium sulphate. The washed precipitate is dissolved in a quantity of pure hydrochloric acid, just sufficient to dissolve it, and again treated with boiling oxalic acid solution, as before. This brings down the rare earth oxalates in sufficiently pure form. The oxalates are thoroughly washed wtih hot water and ignited, and any remaining potassium is separated from the ignited oxides by washing upon a filter with hot water.

With the yttria, as well as the zirconia, physical properties are important, and the oxalate method gives an exceedingly fine precipitate which requires no mechanical treatment.

Experiments indicate that the yttria earths of the greatest atomic weights give the most satisfactory results in glowers. In other words, ytterbia is better than yttria. Owing, however, to the great difficulty of separating the yttria earths from each other, which is so far possible only by laborious fractionation processes, entailing great losses, not much has been done toward using the

higher atomic weight yttria earths beyond selecting ores which are rich in these earths.

The Llano County ores seem to be superior to the foreign ores in this respect, the atomic weights being yttrialite 115, rowlandite 107, fergusonite 103, and gadolinite 100, while the foreign ores may be as low as 90 or 92.

The zirconia and yttria earths mixed in the proportions given above, namely, about 85 and 15, or 90 and 10, and about 5 per cent. of starch or gum tragacanth, are thoroughly mixed and kneaded into a hard dough and squirted by pressure through a die of proper size. This string, as it may be called, is dried and then broken into suitable lengths which are roasted to an intense white heat in a platinum box. The pieces are then ready to have terminals placed upon them.

A Nernst terminal is made by winding stranded platinum wire about the end of the stick of material and then pasting over with a paste composed of ground glowers and zirconium chloride, thus forming a hard cement.

The Hanks terminal has the platinum embedded in the glower material, the operation being carried on by the aid of an electric arc in which the glower material is fused.

It appears certain that the mode of conducting the current is partly electrolytic in character. The specific resistance varies with the relative proportions of the constituents. In order to obtain glowers of the same specific resistance when using yttria earths of high atomic weights as when low atomic weight earths are used, it is necessary to have the presence of the higher atomic weight materials in proportion to the atomic weights.

Upon direct current circuits the positive end of the glower generally runs much hotter than the negative end, and a black discoloration appears at the negative end, especially if impurities are present. In fact, this is one of the most certain indications of the presence of an impurity.

A glower operated in vacuum soon destroys the vacuum, probably due to oxygen gas liberated by electrolytic action. That all the current is carried by electrolytic means seems incredible, for the current carried per square unit of cross-section is far greater than can easily be accounted for by our usual conceptions of electrolytic laws. For example, upon direct current and calculated by electrochemical equivalents the entire glower would be decomposed into the constituent elements in a very few minutes. Doubtless electrolytic decomposition and recombination do take place, but is it possible to account for the entire transport of current in this way? The assumption that the current is all so carried seems unnecessary in view of what is known of the power of highly incandescent bodies to ionize air to render it conducting. The air in the neighborhood of a glower is conducting, and to such an extent that the leakage currents from glower to heater had to be

reckoned with early in the experimental work, and the difficulty was obviated by the use of a double pole cut-out which disconnected the heaters completely from electrical connection with the remainder of the lamp after the glower started.

In connection with these speculations as to the real nature of the process by which the current traverses the glower, it is a fact that glowers which have operated for even a short time upon direct current will, when the current strength is diminished sufficiently to maintain the glower at only a good red heat, explode with considerable violence. This may be accounted for by considering that the conductivity at low temperatures is insufficient to ionize the surrounding and contained gases. The means of conducting the current then being largely electrolytic in character, the combination of the products of electrolytic decomposition cannot so readily take place, since the ions cannot so readily traverse the length of the glower to combine at the lower temperature, and consequently disruption occurs.

The suggestion that has so often been made, namely, that the current be reversed in direction at intervals, as, for instance, every time the lamp is started, is altogether impracticable for the reason that a glower once operated upon direct current must never have its poles reversed, for a reversal means almost instant disruption. The potential difference across the terminals of the glower immediately after such a reversal is lower, indicating something analogous to polarization effects as we know them in aqueous electrolytes.

In general, with the Nernst terminal the potential difference across the glower at the normal current value is the same with alternating or direct current. With the Hanks terminal, or embedded type, the potential difference with direct current may be as much as 20 volts lower. The Hanks terminal will operate on direct current, but not satisfactorily as a commercial proposition. The life of the alternating current glowers is greater upon high frequencies than upon low frequencies, again suggesting electrolytic conductivity, at least in part.

The small glowers, up to 0.5 ampere, are made solid in cross-section, the larger ones are generally made tubular, and, in fact, one-ampere glowers must be made so. The reason for this is not that greater efficiency is sought by increasing the ratio of surface to volume, which is, of course, a fallacy, but inasmuch as the glower possesses a decided negative temperature coefficient as regards electrical conductivity, the center of a large solid glower would become molten before the outside surface reached an efficient temperature, the center being the better conductor. Glowers which have been greatly overrun often exhibit this truth by the appearance of a nodule of molten material which has spurted out to the surface.

Glowers in Vacuum.—A glower will operate in vacuum but the vacuum rapidly deteriorates, as before stated. A blue aurora or luminous haze surrounds the glower thus operated, either with direct or alternating current, and has been thought to be due in some way to vaporized metal (zirconium or yttrium) recombining with the slight amount of oxygen liberated. This idea seems plausible from the fact that objects, such as wire or glass, near the glower become coated with a white deposit of the glower oxides in a comparatively short time.

It would seem that oxygen necessarily plays a part in conducting the current, for a glower in an atmosphere of hydrogen or nitrogen behaves similarly to the one operated in a vacuum. In carbon monoxide or dioxide the glower exhibits the same characteristics as in air. The glower operated in vacuum exhibits a peculiar sluggishness in responding to changes in voltage at its terminals.

A commercial glower must operate at a high temperature to be efficient. Nernst glowers operate at about 2,300° C., it is supposed from determinations made by photometric means and at about twice the efficiency of a carbon incandescent lamp. The spectrum of a glower is a continuous one and no evidences of selective emission in any particular region are noted. During the life of a glower, which averages about 800 hours under normal conditions of manufacture and voltage regulation, a depreciation of candle-power takes place, due to a number of causes. In the first place, all oxides of the rare earths do depreciate rather rapidly in light intensity per unit of surface at any given temperature. This is true even when heated by gas or electricity, and a platinum plate coated on one side with rare earths and heated from the rear by an oxyhydrogen flame behaves similarly. It is an inherent property of these oxides and a depreciation of 10 or 20 per cent. may occur during the first hour. There is then a slow diminution of intensity of light, also inherent, and seemingly accompanying the tendency of the glower to change from an amorphous to a crystalline structure. A rise of potential difference across the glower terminals is usual, though it is possible to counteract this tendency, at least in part. The effect of a rise in potential difference, obviously, is to diminish the intensity of light by permitting less current to traverse the glower running on a constant potential circuit.

With carbon incandescent lamps the useful life or smashing-point is considered to be that number of lamp-hours during which the candle-power decreases 20 per cent. from the initial candle-power. Nernst lamps are similarly rated, counting as initial candle-power that measured after the initial decrease above mentioned.

Another cause of depreciation in candle-power is blackening of the enclosing glassware and reflecting surfaces. In this connection the blackening is due largely to platinum which has been vapor-

ized and deposited upon these surfaces. It has been found that the purest platinum is far better than that containing iridium or other of the platinum group, since pure platinum vaporizes much more slowly than alloys with these other metals.

It is to produce uniform chemicals and glowers in which the tendency to depreciate in light intensity and increase in potential difference shall be a minimum that makes the problem so intricate and so fascinating, and still capable of much improvement.

Curiously enough not the least of the problems to be solved in the development of the Nernst lamp was to overcome the tendency of porcelains to conduct electricity, the very property which in the case of the rare earths made such a lamp as the Nernst possible. A heater is necessary to start the glower. The heater is made by winding fine platinum wire upon a porcelain tube. It was necessary to produce a suitable porcelain which would withstand the high temperatures required and at the same time not conduct electricity. A porcelain composed of kaolin, alumina and silica is sufficiently refractory and porous to withstand the heat and is an almost perfect non-conductor at high temperatures. The porcelain piece upon which the glowers and heaters are mounted is also of the same composition.

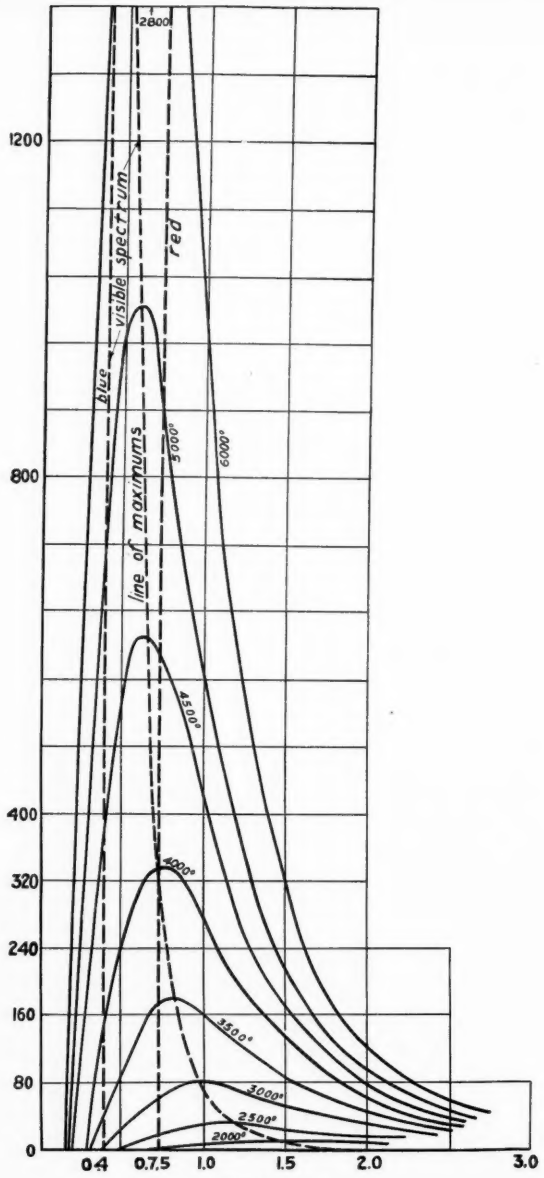
Another form of heater, used more abroad than in this country, is helical in shape, and the glower is mounted in its axis. This is made of pure kaolin and after squirting into tubes about a millimeter in diameter, winding with fine platinum wire and covering over the wire with a paste, the small tube is bent into a helix upon a mandrel, a pointed blowpipe flame playing upon the kaolin tube at the point where it bends on to the mandrel.

Possibilities of Self-starting Filaments.—Many oxides will conduct at room temperature. A mixture of iron and tin oxides, about 70 iron to 30 tin, will start without preliminary heating and withstand rather a high temperature. There are many other similar combinations, likewise other possibilities exist, such as carbides, silicides and borides, operated either in vacuum or gases.

A Nernst glower may be made to conduct the current at low temperatures by running it for a short time in a rarefied atmosphere containing a carbon gas. If to a globe in which a glower is operating in a good vacuum an amount of hydrocarbon gas is admitted sufficient to lower the vacuum even less than a millimeter, the potential difference across the terminals of the glower will decrease rather rapidly and in the space of a few minutes, or even seconds, the glower will have become a conductor when cold or, in other words, self-starting.

The following experiment was tried:

A glower was mounted in a glass bulb and in the axis of a carbon filament of helical shape. The bulb was well exhausted and sealed off. The carbon filament was used four or five times to start the


2800
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160
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visible spectrum
red
line of maximums
6000°
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3500°
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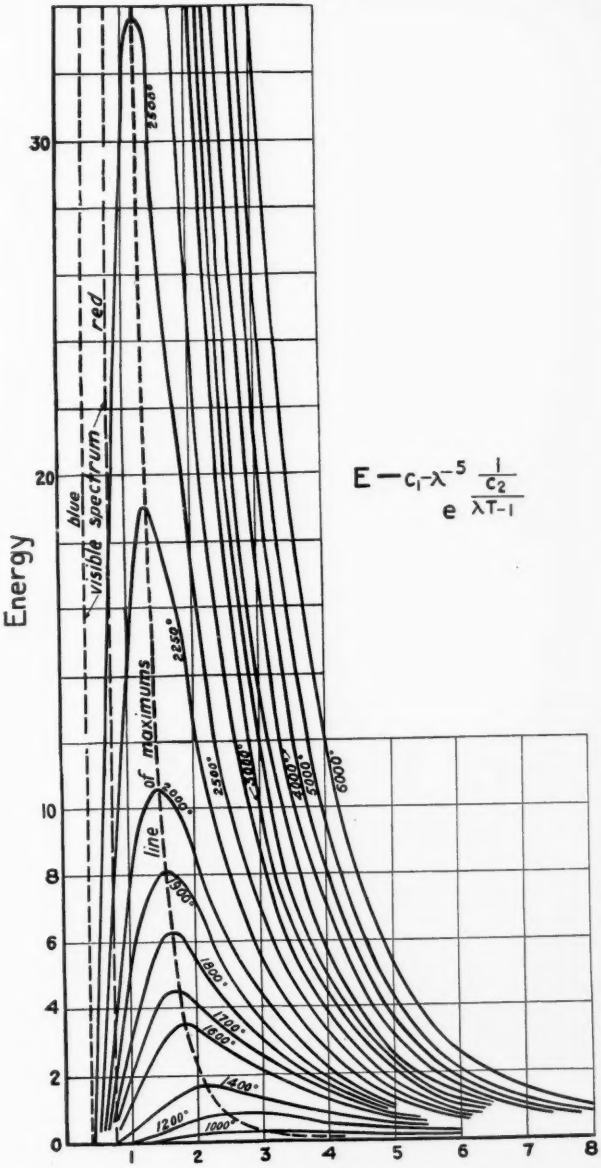
Wave-length.


Energy
Wave-length.
$E = c_1 \lambda^{-5} \frac{1}{e^{\frac{c_2}{\lambda T}-1}}$
blue
visible spectrum
red
line of maximums
2500°
2350°
2200°
2100°
2000°
1900°
1800°
1700°
1600°
1400°
1200°
1000°
0
2
4
6
8
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30
1
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8

glower, alternating current being employed. After the glower had run a few hours it was noted that it was changing color at its terminals. The discoloration gradually crept toward the center and after about twenty-four hours the glower could then be started without preliminary heating. Apparently enough of the carbon filament was oxidized during the short time it was in use to give a slight quantity of free carbon monoxide in the bulb, the source of oxygen being the glower itself.

It is uncertain whether this gas was effective in reducing some of the glower material to its metallic form, or whether a conducting carbide was formed by the action of the carbon gas upon the glower materials. The former explanation seems preferable for the reason that it was noticed that the darkened portion at the negative end of direct current glowers is of higher conductivity than the glower proper, and it seems quite likely that this deposit is a metal separated out by electrolytic action. Metallic zirconium, for example, withstands very high temperatures in the open air without oxidizing, and its melting- and vaporizing-points where air is excluded must be very high.

Many possibilities exist, such as are suggested by the above experiments, and many of them have been tried. Boron carbide, for example, withstands very high temperatures and is a conductor while cold, though it seems to vaporize somewhat too rapidly; at least this was the case with samples tried, which probably were not very pure.

A Nernst glower, as well as those composed of thoria, magnesia, and almost any of the refractory oxides, may be made conducting by treatment with a hydrocarbon gas. Sodium and potassium vapor also affect a reduction to the self-starting condition, though not generally so readily as carbon.

There is a broad field still open and much that is not known of the properties of the rare metals. Oftener than not the supposedly pure metal is very impure, and the properties generally ascribed to it are in reality those of its carbide or other little known combination. Note the difference in properties of pure iron and iron containing even less than 1 per cent. of carbon. Is it not a fact, then, that almost nothing is known of the physical properties of the rare metals? A good example of this point, and one bearing directly on our subject, is the recently developed tantalum lamp, the filament of which is a fine thread of tantalum metal. Tantalum metal, until recently, was not known to possess properties which now make it a promising addition to electric illuminants.

More or less experimental work has been done, particularly in Europe, in using the rare earths in electric arcs with the idea of obtaining better efficiency and more pleasing light. Lamps have even been tried with electrodes composed entirely of the rare earth oxides, though at the present time the greatest advances in arc lighting are being made along the lines of introducing such elements as boron and titanium into the electrodes.

In conclusion, your attention is directed to a set of curves which has been plotted to show the relation between the temperature and the energy radiated in the various wave-lengths of light for incandescent black bodies. Various temperatures are assumed, and curves calculated, showing the energy radiated at each wave-length. The visible spectrum is defined by the vertical broken lines marked red and blue. The exceedingly small proportion of the total energy which is radiated within the limit of the visible spectrum even at a temperature as high as 3500° C., is startling enough. We are, apparently, at the present only on the border of possibilities.

2210 FARMERS' BANK BUILDING,
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NEW BOOKS.

THE PRINCIPLES OF CHEMISTRY. By D. MENDELÉEFF. Third English edition, translated from the Russian (seventh edition) by George Ramensky. Edited by Thomas H. Pope. Longmans, Green & Co. 2 vols. 1190 pp. Price, $10.00.

The third edition of this standard work is a more important revision than its predecessor. The author assures us that "the additions and alterations have, in many instances, cost as much labor as the original compilation." Additions to fact are numerous, among the more noteworthy of which, the liquefaction of gases, the rare atmospheric elements, and the subject of radioactivity, are treated in some detail; but the theoretical portions of the book have acquired a preponderating interest, since they are evidently to be regarded as a final statement of the author's views. His own words are: "In carefully preparing this edition, I have not lost sight of the fact that I am hardly likely to publish another, and I have, therefore, in many instances spoken more definitely than formerly." Many of these views have already been published singly, but this is the first time they have appeared together as parts of one whole.

The periodic system is enlarged by the addition of a zero group (of zero valence) embracing helium and the rare gases of the air. Regarding former discrepancies in the periodic table, Mendeléeff reaffirms his belief that the order I–Te, Ni–Co, K–Ar will eventually be reversed. The position of the rare earths is still problematic. Brauner, who contributes a chapter on the subject, presents his view, previously published elsewhere, that these elements taken together form a division occupying a single space in the table, sustaining a relation similar to the elements of Group VIII.

Mendeléeff's views of solutions have not changed, but his

objections to present theories are stated with greater distinctness. While he recognizes the great fertility of Arrhenius' hypothesis, he says: "The return of electrochemism which is so evident in the supporters of the hypothesis of electrolytic dissociation, and the notion of a splitting up of atoms into electrons, in my opinion only complicate and in no way explain so real a matter as the chemical change of substances." His call for a theory which accounts for the chemical process of solution will find a ready response, yet his own conception as before fails to fit the facts in any such detailed way as to carry conviction.

In more than one place, the author takes occasion to assert emphatically his disbelief in a primary matter, however strongly some of his own discoveries would seem to point in that direction. "The more I have thought on the nature of the chemical elements, the more decidedly have I turned away from the classical notion of a primary matter, and the hope of attaining the desired end by a study of electrical and optical phenomena."

Perhaps the most remarkable thing in the book is Mendeléeff's attempt to identify the ether with the lightest of all gases and the first member of the zero group, of enormous molecular velocity, molecular size correspondingly minute, and devoid of combining power. Inasmuch as this conception is largely the result of extrapolation over a long range, the conclusions are correspondingly hazardous. Minor errors in a work of this character scarcely deserve a place in a review of this scope.

EUGENE T. ALLEN.

COURS DE CHIMIE. A L'USAGE DES ETUDIANTS DU P. C. N. PAR R. DE FORCRAND. Paris: Gauthier-Villars. 1905. Vol. I, 325 pp. Vol. II, 317 pp. Price, 10 Francs.

In these volumes the author presents a course in chemistry, that he proposes to teach in one year, allowing three lessons to each week. Forty-eight pages in the first volume suffice for a discussion of general principles, laws, etc.; then follows a systematic treatment of the *metalloids* and *metals*. Organic chemistry occupies two-thirds of the second volume, while the remaining 100 pages give an outline of analytical chemistry.

This work may be of value to the special class of students for which it was written, but for general use it leaves much to be desired. Certainly many teachers will object to a discussion of general principles before any of the simple facts of chemical action

have been learned. The treatment of the topics is frequently so meagre that even an advanced student would have difficulty in comprehending it. The periodic law, the ionic theory, the Kjeldahl method for the determination of nitrogen and many other important subjects are either not mentioned, or are skilfully concealed. There are so many good text-books in English, French and German, that this new candidate for favor seems unlikely to secure a prominent place. L. B. HALL.

THEORETICAL CHEMISTRY FROM THE STANDPOINT OF AVOGADRO'S RULE AND THERMODYNAMICS. By WALTHER NERNST. Revised in accordance with the fourth German edition by R. A. LEHFELDT. xxiv + 771 pp. London: Macmillan & Co.; New York: The Macmillan Co. Price, $3.75 net.

No English translation of this standard work upon the general principles of chemistry and upon physico-chemical relations has appeared since shortly after the issuance of the first German edition in 1893. Since that time the original work has been so much modified and extended that the former translation has become entirely antiquated, and that the present one may be regarded as substantially a new book. It is, therefore, not worth while to review in detail the differences between the two publications. It will suffice to call attention to the fact that the English reader has now available to him a translation of the most recent edition of one of the leading German works upon theoretical chemistry—a work which is of great value for purposes of reference, and which as a textbook is especially suited to the somewhat advanced student who wishes to make a fairly thorough study of the subject. The translation of the portions of the book added or rewritten since the first edition is fairly satisfactory; that of the original portion, which unfortunately was only partially revised by the new translator, is often scarcely intelligible. A. A. NOYES.

STUDIES IN GENERAL PHYSIOLOGY. By JACQUES LOEB, formerly of the Department of Physiology in the University of Chicago; Professor of Physiology in the University of California. Decennial Publications of the University of Chicago, Second Series, Volume XV. In two volumes. Chicago: The University of Chicago Press. 1905. 782 pp. Price, $7.50 net.

The appearance in book form of the brilliant work of the author along the lines of general physiology will be welcomed by physiologists and other scientific men, who are in touch with physiological literature. So many popular accounts have appeared from sensational journalists, without Loeb's knowledge or consent, that

many would like to know exactly what he has accomplished. We have here a republication of 28 of the most important original articles, which appeared from the author from 1889 to 1902, in various German and American journals. Preliminary notices and communications, which appeared in collaboration with assistants and students, have been omitted in this publication. The German articles have been translated into English. It is, of course, impossible to discuss Loeb's work within the limits of this review, but the fields of his activity may be gathered from the following general topics: Heliotropism, heteromorphism and geotropism in animals; regeneration, the part played by the nucleus in cell oxidation; salt action; fertilization. It is interesting to note that Loeb has received the inspiration for much of his work from two related sciences. His beautiful early work on heliotropism and geotropism was apparently inspired by the corresponding work of Sachs on the botanical side. He showed that the laws laid down by Sachs for sessile plants hold perfectly for some of the lower forms of animal life as well. From this work the investigations on heteromorphism, regeneration, will and instinct developed. Then again, his work on salt action was apparently stimulated by the rise of the ionic theory of solution. Decidedly the most striking and far-reaching of his experiments are those on parthenogenesis, which are certainly epoch-making. He succeeded in producing normal larvae from the unfertilized eggs of the sea urchin. He found that an increase in the concentration of the sea-water as well as slight changes in the reaction could bring about this parthenogenesis. Later, the experiments on artificial parthenogenesis were extended to annelids. The subjects are written up in such a broad and highly suggestive way as to make them most readable. Loeb is at present too young and too vigorous an investigator to have his place among physiologists assigned to him, as we know not what he has in store for us. His work has, however, placed him in the foremost rank as an investigator, and his influence has been widely felt in physiology and the related sciences. This work would be a valuable addition to any physiological or biological library.

A. S. LOEVENHART.

FIRE ASSAYING NOTES. BY F. P. DUNNINGTON, School of Analytical Chemistry, University of Virginia. 1905. Easton, Pa.: Eschenbach Printing Company.

This pamphlet is in the nature of a syllabus, no doubt designed

to give the subject-matter of a series of lectures in a course of assaying. Every other leaf is blank for the purpose of making notes by the student. It contains nothing new, and the presentation of the subject is not always satisfactory, and sometimes misleading; for instance, on page 7 the very inaccurate method of Berthier is given "to obtain the heating power of coal," and on page 8 the author says, "clay may be recognized by stirring the finely powered ore in water."

In the formulae for fire-assaying for gold and silver the quantity of ore to be used, in every case, is given in even numbers of grams, instead of so many assay tons or fractions thereof, as is now universally the practice, so that while this outline may be suggestive to those teaching the subject there seems nothing about it which particularly commands commendation. WM. HOSKINS.

THE CHEMICAL SYNTHESIS OF VITAL PRODUCTS, AND THE INTER-RELATIONS BETWEEN ORGANIC COMPOUNDS. BY RAPHAEL MELDOLA, F.R.S., V.P.C.S., F.I.C., etc., of the City and Guilds of London Technical College, Finsbury, etc. Volume I, Super Royal, 8vo. pp. xvi + 338. London: Edward Arnold. 1904. Price, $6.00 net; by mail, $6.22.

CONTENTS: Introductory. I, Historical. II, Nature of the Compounds Registered as Vital Products. III, Organic Chemistry from the Biocentric Standpoint. IV, Chemical Synthesis from the Biocentric Standpoint. V, Advantages of the Biocentric Treatment of Synthetical Chemistry. Hydrocarbons. Alcohols and Terpene Alcohols. Ketone Alcohols. Glycols and Polyhydric Alcohols. Aromatic Alcohols and Phenols. Aldehydes and Ketones: Fatty Group. Aromatic Aldehydes and Ketones. Carbohydrates and Glucosides. Sulphur Compounds. Cyanogen Compounds. Appendix: Camphor and Terpene Group; Flavone Group.

This work, upon which the author has been engaged for the past nine years, is a compilation of all those products of vital activity, which have been prepared synthetically. The natural sources and methods of synthesis are fully set forth, and, as the methods are given by which the generators of these vital products are obtained, the syntheses are in every case complete.

The author recognizes as "vital products" those "compounds of definite chemical composition which are known to be produced as the result of the vital activities of animals and plants, including micro-organisms," and the term "synthesis" is used to indicate both up-grade and down-grade processes. Reactions and schematic representations are omitted, to make the work more compact, but the arrangement of the substances is such that their genetic relations appear very clearly.

It is essentially a reference work, not merely a catalogue of synthetic products and processes, nor a laboratory guide for the preparation of organic compounds, nor is it, in any sense, a critical treatise. On examining its pages, the organic chemist will be surprised to see how many carbon compounds may properly be classed as vital products, 181 being described in the present volume, and the physiologist will be impressed by the number of vital products which have been synthesized by the chemist.

The author calls attention to the many points of interest brought out by this biocentric treatment of carbon compounds. Thus, while it is quite true that we can produce in the laboratory substances identical with those formed in the living organism, in the majority of cases we cannot maintain that the syntheses are identical in their mechanism, and those who would 'explain' the biochemical processes by a simple chemical equation should bear in mind the fact that "the sign connecting the two sides of the equation stands for the whole unexplored region of biochemical transmutations." We lack exact knowledge of the nature of the synthetic processes going on in the living organism, and there is little reason for believing that they have much analogy with our laboratory methods. In fact, we cannot duplicate in the laboratory the most fundamental of all these syntheses—the photosynthesis accomplished by plants, in which carbon dioxide is absorbed by an organic compound, and the product decomposed with liberation of oxygen. While the author does not at all intend to array himself on the side of the Vitalists, he concludes, from the summary of experimental results recorded in this book, that "the testimony of pure chemistry cannot, as it stands at present, be legitimately interpreted into a direct negation of Vitalism in any form. This negation may, and probably will, be made possible in the future, when our chemical methods have been made to approximate more closely to the vital methods."

Although many definite vital products have been isolated, identified, and synthesized in the laboratory, the manner in which these compounds are produced in the organism can hardly yet be said to have been satisfactorily traced in any single instance. Such a problem is for the physiologist to solve rather than the chemist, but the best results in investigations of this character would naturally be secured by the two working together, and the

author expresses the hope that his book may lead to some such co-operation.

A fact of historical importance, and one which has generally been overlooked by the authors of text-books and reference works is prominently set forth here, with the necessary documentary proof. This is that the Englishman Hennell synthesized alcohol from ethylene at about the same time that Wöhler prepared urea from ammonium isocyanate. Although Berthelot has disputed Hennell's claim, the evidence cited seems to show quite clearly that Hennell prepared alcohol synthetically several years before Berthelot.

The subject-matter is arranged on the page in double columns, and after every compound are given (*a*) Natural Sources and (*b*) Synthetical Processes. The references to the literature are complete up to the close of 1902, and the Index is very extensive. A second volume will complete the work. It should prove a very valuable compilation for all organic and physiological chemists.

MARSTON T. BOGERT.

THE CHEMISTRY OF GAS MANUFACTURE. By W. J. A. BUTTERFIELD. Third Edition. Vol. I. 1904. 257 pp. Illustrated. London: Griffin; Philadelphia: Lippincott. Price, $2.50.

This is the best of the smaller works on the subject of gas manufacture. The first edition appeared as a single volume in 1896.

The present volume treats of Materials and Processes, while the second will discuss Gas Analysis, Photometry, Calorimetry, and the Uses of Gas. In the chapter on raw materials the author describes the various substances used, and also gives some good methods for their valuation.

Coal-gas and its purification come in for nearly one-half of the volume, following which is a short chapter on water-gas and another on oil-gas.

Experience in a country where carburetted water-gas is more generally distributed than it is in England would lead the author to modify the statement that "the danger of accidental poisoning from carburetted water-gas is virtually confined to the works where it is made."

The book is well printed, and while it was intended primarily for the gas works laboratory, it will be found a useful addition to the library of every chemist.

E. G. LOVE.

EXERCISES IN PRACTICAL PHYSIOLOGICAL CHEMISTRY. By SYDNEY W. COLE. Cambridge: W. Heffer & Sons. London: Simpkin, Marshall & Co. 152 pp. Price, 5 shillings, net.

This is a very good little book for laboratory work and comprises more than is usually given to students in physiological chemistry. Its chief merit is found in the fact that it is written by a man who is familiar with the modern views of the protein and other groups of physiologically important substances. The directions for manipulations are plain and the explanations of reactions concise and accurate. J. H. LONG.

PRACTICAL EXERCISES IN CHEMICAL PHYSIOLOGY AND HISTOLOGY. By H. B. LACEY AND C. A. PANNETT. Cambridge: W. Heffer & Sons. London: Simpkin, Marshall & Co. 112 pp. Price, 2 shillings, net.

This book contains directions for a very large number of laboratory experiments, most of which appear to be satisfactory. The work, however, is given in the routine way popular with some teachers and many of the pages are divided in parallel columns headed: *Experiment, Observation, Inference.* The book appears to be intended for students who are working for "honours" in physiology examinations. J. H. LONG.